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FEASIBILITY STUDY OF REGENERATIVE FIBERS FOR WATER POLLUTION CONTROL

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16. Abstract: High molecular weight organic polymers co-spun with fiber-forming polymers and cross linking agents have been successfully spun into fiber and chemically treated to produce ion exchanging fibers, as opposed to the conventional beads. Styrene sulfonic acid cation exchange fibers, having capacities up to 4.2 meg/gm dry fiber were prepared, using polypropylene and polybutadiene as fiber-forming polymer and cross linking agent respectively. By cutting the fibers to very short lengths, it was possible to test these materials by column elutions, with breakthrough capacities for ion exchange fibers demonstrated to be higher than those for beads, possibly due partly to a higher exchange rate in the fibers. Selectivities of fibers were similar to those of conventional beads, but different selectivities for the fibers may be possible due to anisotropic swelling of the fibers. Several other types of fibers were successfully fabricated, and further testing as to rate of attrition, effects of organic foulants, and physico-chemical studies of rates and selectivity should be performed. (Lowry-Texas)

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FEASIBILITY STUDY OF REGENERATIVE FIBERS FOR WATER POLLUTION CONTROL

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ABSTRACT

The feasibility of making fibers which have the ability to sorb minerals from water has been investigated. High molecular weight organic polymers cospun with fiber-forming polymers and crosslinking agents can be spun into fiber and chemically treated to give ion exchanging materials. In some cases the ion exchange active material can be spun directly (e.g., polyamines and polyvinylpyridines); in other cases the activity must be introduced after spinning (e.g., the sulfonation of fibers containing polystyrene).

Styrene sulfonic acid cation exchange fibers having capacities up to 4.2 meq/g dry fiber have been prepared. Polypropylene and polybutadiene served as fiber-forming polymer and crosslinking agent, respectively.

By cutting the fiber to very short lengths, it was possible to test these materials by column elutions in much the same way as conventional ion exchange beads are evaluated. Accordingly, the breakthrough capacities for ion exchange fibers were found to be higher than those for beads, probably due in part to a faster rate of ion exchange in fibers.

Weak acid cation exchangers were produced from fibers containing polymethylmethacrylate by hydrolysis of the ester to polymethacrylic acid. Capacities up to 1 meq/g were obtained.

Vinylpyridine and aliphatic amine ion exchange active materials were spun directly and then crosslinked with dihaloalkanes. Quaternization was achieved with alkyl halides. Vinylpyridine exchangers gave capacities up to 3.8 meq/g, and fibers containing both vinylpyridine and polyethyleneimine show promise of yielding higher capacities.

Selectivities of ion exchange fibers were similar to those of conventional beads, but different selectivities may be possible because of the anisotropic swelling of the fibers.

This report was submitted in fulfillment of Project Number 17040 DFC, Contract 14-12-815, under the sponsorship of the Water Quality Office, Environmental Protection Agency.

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SECTION I

CONCLUSIONS

1. The feasibility of using high molecular weight organic polymers cospun with fiber forming polymers and crosslinking agents to sorb minerals from water has been established.

2. Ion exchange fibers can be made strong and durable while maintaining high percentages of active material in the fibers.

3. Selectivities of ion exchange fibers parallel those of conventional beads; however, different selectivities may be possible because of the anisotropic swelling of the fibers. Based on theoretical considerations and indirect experimental evidence, the rates of ion exchange for fibers are concluded to be much greater than corresponding rates in beads.

4. Styrene sulfonic acid cation exchange fibers having capacities (4.2 meq/g dry fiber) of comparable magnitude to those of conventional ion exchange beads can be produced. Polymerized butadiene serves as a crosslinking agent for the styrene sulfinic acid exchangers.

5. Weak acid cation exchangers may be produced from fibers containing polymethylmethacrylate by hydrolysis of the ester to polymethacrylic acid.

6. Vinylpyridine and aliphatic amine ion exchange active materials may be crosslinked with dihaloalkanes. Quaternization may be achieved with alkyl halides. Vinylpyridine exchangers having capacities of 3.8 meq/g dry fiber can be made. Fibers containing both vinylpyridine and polyethyleneimine show promise of yielding higher capacities.

SECTION II

RECOMMENDATIONS

This research was restricted to determining the feasibility of making ion exchange fibers of reasonable capacity and strength. Pursuant to a fuller understanding of the properties and potential applications of these ion-sorbing fibers, the following program is recommended:

1. Existing fibers should be thoroughly tested for rate of attrition by following the capacity over a large number of exhaustion-regeneration cycles.

2. The effect of organic foulants on ion exchange fibers should be determined. Also the effect of fiber porosity on organic fouling should be determined. Some of these tests should be made using actual secondary effluents.

3. Physico-chemical studies of rates and selectivity should be performed on ion exchange fibers under conditions simulating actual operations, and these results should be compared with those for ion exchange beads.

4. A bench scale model of a continuous ion exchange system utilizing a moving belt fabricated from ion exchange fiber should be constructed. The belts could be tested for rates of exchange, selectivity, attrition, and fouling.

5. Improved ion exchange fibers should be sought -- fibers having maximum ion exchange capacity while keeping maximum strength.

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SECTION III

INTRODUCTION

As our population grows and the per capita water requirements likewise grow, it has become apparent that within the next two decades the daily need for water will exceed our fresh water resources. Long before this high demand for water is reached, it will not be practical to discharge secondary effluents into streams; "purification by dilution" will no longer be effective. Not only will tertiary treatment be necessary before discharge into rivers and streams but in some cases water will have to be conditioned for immediate reuse. In order to promote widespread application of tertiary treatment, a highly advanced technology must be developed -- especially toward reducing the cost of waste water renovation for reuse.

Four distinct processes have evolved as the most feasible for demineralization of waste water. These are distillation, electrodialysis, reverse osmosis, and ion exchange. A number of variations and combinations of these basic processes have been proposed. Clearly, all of the above methods of water treatment have both technological and cost deficiencies.

Ion exchange has been most successful in applications requiring the demineralization of water having reasonably low levels of organic pollutants and has been used widely in the treatment of industrial wastes. Irreversible fouling by organic contaminants has been greatly reduced by improved ion exchange resins, and ion exchange processes have been successfully demonstrated for the treatment of secondary effluents (1). Although ion exchange processes are generally regarded to be most economical for low solids water, improved processes have been developed for water with high total dissolved solids including desalinization of sea water (2).

Ion exchange as a unit operation requires periodic regeneration of the exchanger. Thus, two ion exchange systems are necessary in order to maintain continuous demineralization. On the other hand, continuous ion exchange systems are rather complex and require costly plumbing for transport of the resin from the exhaustion column to a regeneration compartment and back. Attrition of the ion exchange resin is higher than in conventional fixed-bed equipment (3). Another difficulty in continuous ion exchange systems is maintaining column integrity while moving the resin. It is desirable, then, to consider forms for ion exchange materials which differ from the usual spherical bead and are more amenable to continuous operations. Three fundamental shapes can be distinguished -- the bead (usually spherical), the fiber (one dimension much larger than the other two), and the film (two dimensions much larger than the third). Ion exchange films or membranes are employed in elec-

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trodialysis and various other applications. The films are generally weak and are not suitable in applications involving mechanical movement. Ion exchange fibers could be practical for column operations since the fibers (in the form of a bundle of cylindrical lengths) pack more efficiently than spherical beads. Furthermore, ion exchange fibers can be woven into tough, durable materials capable of withstanding the duress of continuous mechanical movement. A strong belt can be fabricated from very thin fibers, thus exposing a very large surface area of ion exchange material.

The requisite physical properties for an ion exchange fiber differ greatly from those for the conventional ion exchange bead. Whereas the beads are hard and brittle, the fiber must be flexible and elastic. For this reason the chemical composition of an ion exchange fiber will likely differ from that of spherically shaped ion exchange materials.

An ion exchange fiber is composed of three basic elements: (1) an ion exchange active material, (2) a fiber forming resin, and (3) a crosslinking agent. A given chemical constituent in the fiber may serve in one or more of the three categories. Certain ion exchange active material can be melt spun with a fiber forming polymer. However, highly ionic materials usually cannot be melt spun, and for these cases the ion exchange activity must be introduced by chemical reaction after spinning. The chemically active groups suitable for ion exchange fibers are identical to those available in conventional ion exchange beads. Moreover, the chemical framework to which the exchange active groups are attached is often similar in fiber and beads. For example, the skeletal structure for a sulfonic acid cation exchanger might be polystyrene in both fiber and beads.

In general, neither the organic polymers with ion exchange capacity nor those polymers which are converted to ion exchangers after spinning will form strong fibers. Therefore, it is usually necessary that part of the ion exchange fiber be composed of a strong fiber forming material (for example, polyolefin, polyamide, polyester, etc.). As little as ten percent of this inert fiber forming polymer in the ion exchange fiber can improve its strength by more than a factor of ten. The amount of inert filler in the ion exchange fiber is a compromise between fiber strength and loss of total capacity since these fiber forming resins have no sorption capacity.

The third major ingredient of the ion exchange fiber is the crosslinking agent. It is not possible to spin crosslinked material, and the actual crosslinking must be effected after spinning. In conventional ion exchange beads, crosslinking is often achieved at little expense to total capacity. For example, in a styrene polymerization the divinylbenzene added for crosslinking may be sulfonated with the styrene to produce additional cation exchange sites. Thus, any loss in theoretical capacity is due only to the small difference in the equivalent weight of styrene and divinylbenzene. In contrast to the above efficient

crosslinking system, crosslinking in ion exchange fibers often requires a material which has no capability for conversion to ion exchange activity, and in such cases the crosslinking agent significantly reduces the maximum theoretical total capacity. However, the presence of an inert fiber forming material and the usually high degree of crystallinity in the fiber allow for the use of less crosslinking agent than would otherwise be required.

Some early work in the use of fibrous materials for ion exchange was presented by Muendel and Selke in 1955 (4). The ion exchange fibers reported were exclusively chemically treated natural fibers. Since this preliminary work, very little has appeared in the literature with the exception of several patents (5-7). The purpose of the present study was to determine the feasibility of using melt-spun polymers for the removal of ions from water and waste water. Melt spun fibers have the potential advantage of greater capacity and lower cost. The study included the preparation of multicomponent fibers which function as ion exchangers and the evaluation of these fibers in column operation for comparison with conventional bead ion exchangers.

SECTION IV

EXPERIMENTAL

PREPARATION OF ION EXCHANGE FIBERS

All fibers were spun from the melt in a 1-inch Modern Plastics Machinery Co. extruder feeding a size 1/2 gear pump. The melt emerged from an eight hole die (0.020 in. hole diameter) at temperatures ranging from 230° to 260°C and at a rate of about 5 g/min. The fiber was taken up at 200 to 300 ft/min. Prior to spinning, the ingredients were thoroughly mixed by one of three methods depending on their physical state and stability. If all the ingredients had approximately the same small particle size, mixing was readily achieved at room temperature on a ball mill. Those ingredients having disparate particle size or requiring mixing of solids and liquids were banded on a steam heated two-roll mill and ground in a Cumberland grinder. Alternatively, for mixtures lacking the oxidative stability for mill mixing at elevated temperatures, the ingredients were extruded through a single hole (1/8 in. diameter) die at 230° to 260°C and chopped to produce pellets about 1/4 in. long. For materials which were easily degradable, the extrusion operations were carried out under an argon atmosphere. Whenever possible the fiber strength was increased by hot drawing. The fiber, entering a 130-150°C oven at a fixed rate, was drawn from the oven at a faster rate, the ratio of speeds being the draw ratio. Because most of the fibers prior to drawing were very weak, the speed at which the undrawn fiber could be fed into the oven was usually less than 50 ft/min.

After spinning, the next step in the preparation of ion exchange fibers is to introduce sufficient crosslinking in the fiber to render it water insoluble and prevent excessive swelling. Two crosslinking methods were employed for most of the ion exchange fibers - one for cation exchangers and one for anion exchangers. The use of these two methods lay partly in their simplicity and partly because the crosslinking agents did not add excessive inert weight to the fiber.

Cation exchange fibers were crosslinked by tying together polybutadiene units which were included in the original fiber mixture. That is, styrene-butadiene copolymers (SBR), acrylonitrile-butadiene (NBR) copolymers, acrylonitrile-butadiene-styrene (ABS), or some combination of the above was spun with the original fiber. Points of unsaturation were then linked by free radicals initiated by cold sulfuric acid or tertiary-butyl peroxide. In the sulfuric acid cure the fiber was placed in conc. H_2SO_4 at 0°C for several hours after which the temperature was allowed to rise to that of the room. The fiber remained in the sulfuric acid at ambient temperature for periods varying from a few hours to several days. This procedure resulted in a small amount of sulfonation as well as crosslinking. Several hours exposure to a methanol or ethanol solution of t-butyl peroxide at room temperature also effectively

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linked points of unsaturation in fibers containing polybutadiene.

All of the anion exchange materials were of either aliphatic amine or pyridine type. Crosslinking these materials was effected by quaternization with dibromoalkanes, typified by the reactions:

$$R_3N + Br(CH_2)_6Br \longrightarrow [R_3N^+ (CH_2)_6Br]Br^-$$

$$[R_3N^+(CH_2)_6Br]Br^- \quad R_3N \longrightarrow [R_3N^+(CH_2)_6N^+R_3]\ 2Br^-$$

Several days exposure to a decane solution of dibromoalkanes at 50°C was sufficient for corsslinking polyvinylpyridines but the method was not as successful in the crosslinking of polyethyleneimine - some of which was always extracted from the fiber during evaluation.

For the weak base ion exchange fibers, crosslinking was the last step in the preparation since mixtures containing the exchange active ingredient could be spun directly. To make a strong base ion exchange fiber, the weak base fiber was further quaternized with a bromoalkane (usually n-bromobutane).

Another crosslinking method attempted for both anion and cation fibers was exposure to high energy electrons. Several samples were irradiated with a Van de Graaff generator electron source (about 1.5 Mev); exposures were between 8 and 32 watt-hr.

Cation exchange materials could not be spun directly, and the activity had to be introduced after spinning and crosslinking by chemical reaction. Strong acid exchangers were made by sulfonation of fibers containing polymerized styrene. Fuming sulfuric acid and chlorosulfonic acid were the sulfonating agents of choice. Rinsing of the fiber after sulfonation must be carried out very carefully in order to avoid charring or even melting of the fiber by the large heats of mixing of the acids with water.

Weak acid cation exchangers were prepared by the hydrolysis of a polyester such as polymethylmethacrylate. Hydrolysis of the ester and crosslinking of butadiene in the fiber were accomplished simultaneously with sulfuric acid.

EVALUATION OF ION EXCHANGE FIBERS - PHYSICAL PROPERTIES

Several parameters relating to physical properties of the fibers were measured after spinning and also after drawing. The properties measured were (a eight-filament denier, (b) percent elongation at break, and (c) tenacity (8). The eight-filament denier is defined as the weight in grams of a 9000 meter length of eight filament yarn. The eight-filament denier is related to the monofilament diameter by

$$\text{diameter (in.)} = 1.65 \times 10^{-4} \sqrt{\text{denier}},$$

assuming the fiber density to be 1 g/cm^3. For example, a denier of 400 corresponds to a monofilament diameter of about 0.0033 in. Denier is measured by weighing a three meter length of fiber. The percent elongation and tenacity are derived from Instron data in which two-inch lengths of eight filament yarns are pulled apart at a constant rate and the load-extension curve recorded. Percent elongation is derived from the length of the fiber just prior to breaking. The relationship between the tenacity in grams/denier and the tensile strength is:

$$1 \text{ g/denier} = 12{,}800 \text{ psi},$$

again with the approximation that the density of the fiber is 1 g/cm^3.

Another physical property which is important in the ion exchange fiber is the degree of swelling in aqueous solution. In many cases the swelling was simply estimated by visual inspection. For finely cut fiber the swelling could be estimated by measuring the volume occupied by the fiber in a column. For more accurate determination of the degree of swelling the fiber was photographed in the wet and dry states at a magnification of about 40X. The fiber diameters were measured to determine the degree of swelling on the assumption that the increase in fiber length was negligible.

EVALUATION OF ION EXCHANGE FIBERS - CHEMICAL PROPERTIES

Generally, the first test made on an ion exchange fiber was a determination of the total capacity. For the strong acid or strong base ion exchange fibers the total capacity was determined by simple acid-base titration. An excess of sodium chloride was added to the fiber in an aqueous solution. The acid liberated in exchange for sodium ions by the cation exchanger is titrated with sodium hydroxide. Similarly, the base liberated in exchange for chloride ions is titrated with hydrochloric acid. In the case of weak acid or weak base ion exchange fibers, the total capacity was estimated by back titration after neutralization of the exchanger. Thus, a known excess of base is added to the weak acid ion exchange fiber, and after a few minutes of contact the fiber and solution are separated. Then the excess base is back titrated to neutralization with acid. The meq of acid subtrated from the meq base gives the total capacity of the fiber.

In order to determine the rate of attrition of the ion exchange fibers, the total capacity was followed as a function of the number of cycles. For strong acid exchangers this was accomplished by the simple titration method; for weak base exchangers the total capacity was derived from column elution data.

All of the column elutions were carried out in 100 ml burets having cross-sectional area of 1.9 cm^2. Finely cut fiber was packed in the buret with a glass plug below and above the fiber. The fiber was cut either by hand, in a Waring blender, or in a Wiley mill. Hand cutting, though tedious, yielded the best samples because the blender and mill tended to crush and disintegrate the fiber.

General performance of the exchangers was tested by elution with calcium ion solutions for cation exchangers or chloride ion solutions for anion exchangers. The effluent entered a siphon cup which delivered volumes ranging from 16 to 20 ml to a fraction collector. Selected effluent samples were then analyzed for the ions of interest. The influent solution was gravity fed to the column and the rate of elution was adjusted by the buret stopcock.

Those elutions for determining ion selectivity required solutions with two ions present, for example, chloride and phosphate. In the case of phosphate and ammonium the second ion was separately analyzed, but in the elution of a chloride-nitrate solution the nitrate ion concentration was known only in the influent solution.

Ion concentrations were determined as follows:

Calcium - EDTA titration, Eriochrome Black Indicator (9)

Chloride - $AgNO_3$ titration, $CrO_4^{=}$ Indicator

Phosphate - Absorption at 880 mμ of an antimony-phosphate-molybdate (10) ascorbic acid complex

Ammonium - absorption at 425 mμ of nesslerized ammonia solution

SECTION V

RESULTS AND DISCUSSION

FIBER SPINNING

A complete list of the mixtures which were formulated for melt spinning is given in Tables 1 through 7. A description of the materials corresponding to the codes used in these tables is given in the Glossary. Physical properties of the fibers are given in Tables 8 and 9. A discussion of the principal characteristics of the fiber formulations and physical properties follows.

Polypropylene-Polystyrene Mixtures

It is clear from Table 1 that polypropylene (PP) and polystyrene (PS) can be spun in all proportions. PS is a fiber forming material, but the filaments are very weak. Thus, a decrease in tenacity with increasing PS content is noted for these compositions. Sulfonation of the fibers in Table 1 will give a sulfonic acid cation exchanger. Only very low ion exchange capacities are possible with these fibers because of the solubility of sulfonated polystyrene. To a small extent the polypropylene prevents extraction of the PS so long as the degree of sulfonation is quite low. Signer et al. (11) have reported that 10% sulfonation renders polystyrene water soluble.

Table 1

Polypropylene-Polystyrene Mixtures

Code No.	% PP	% PPP	% PS
MS-WP-OA	90		10
MS-WP-OB	50		50
MS-WP-OC	10	10	80
MS-WP-OD	10		90

Mixtures Containing Butadiene

In order to prevent extraction of water soluble polystyrene sulfonic acid, butadiene was included in the fiber formulations; crosslinking was then effected via the points of unsaturation after spinning. All of the mixtures in Table 2 contain butadiene in the form of a copolymer or polymer blend. In Table 3 the mixtures of Table 2 which could be melt spun are resolved in terms of inert, styrene, and butadiene content.

The PP-PS-ABS system (MS-WP-8A to -8G) yields good fibers throughout a wide variation in concentrations. The mixture MS-WP-8E was prepared with

Table 2

Styrene-Butadiene Mixtures

Code No.	% PP	% PS	% ABS	% SBR	% NBR	% PMS	% SB-1	% SB-2	% SB-3	% NW
MS-WP-8A	40	50	10							
8B	30	50	20							
8C	20	40	40							
8D	30	40	30							
8E	25	40	35							
8F	25		75							
8G	20		80							
MS-WP-21			100							
MS-WP-26A	20	70		10						
26B*	20	60		20						
26C	15	70		15						
26D*	15	65		20						
26E*	20	60		20						
26F*	30	55		15						
26G*	25	55		20						
26H	30	50		20						
26I*	20	64		16						
MS-WP-31A*			90	10						
31B			92.5	7.5						
31C			95	5						
31D			97.5	2.5						
31E*			85	15						
31F*			80	20						

* Could not be melt spun

Table 2 (Cont.)

Code No.	% PP	% PS	% ABS	% SBR	% NBR	% PMS	% SB-1	% SB-2	% SB-3	% NW
MS-WP-33A	15	40	35	10						
33B	25	45	20	10						
MS-WP-34A			90		10					
34B			85		15					
34C*			80		20					
34D*			82		18					
MS-WP-48A	15		80		5					
48B	10		80		10					
48C	5		85		10					
MS-WP-40A*	15	60			20					
40B	25	65			15					
MS-WP-49A*	25				15	65				
MS-WP-7A*	30	30							40	
MS-WP-29A*	15						85			
29B*	30						70			
MS-WP-30A*	20							80		
MS-WP-32A*	25		37.5				37.5			
MS-WP-45A*	20							60		20

*Could not be melt spun

Table 3

Fiber Compositions in Terms of Major Components

Code No.	% Inert	% Styrene	% Butadiene
MS-WP-8A	41.6	57.7	0.7
8B	33.2	65.4	1.4
8C	26.4	70.8	2.8
8D	34.8	63.1	2.1
8E	30.6	67.0	2.4
8F	37.0	57.8	5.2
8G	32.8	61.6	5.6
MS-WP-21	16.0	77.0	7.0
MS-WP-26A	20.0	72.5	7.5
26C	15.0	73.8	11.2
26H	30.0	55.0	15.0
MS-WP-31B	14.8	73.1	12.1
31C	15.2	74.4	10.4
31D	15.6	75.7	8.7
MS-WP-33A	20.6	69.4	10.0
33B	28.2	62.9	8.9
MS-WP-34A	15.9	69.3	14.8
34B	15.8	65.5	18.7
MS-WP-48A	28.6	61.6	9.8
48B	24.3	61.6	14.1
48C	20.1	65.5	14.4
MS-WP-40B	27.2	60.0	12.8

Table 4

Mixtures with Epoxy Resin

Code No.	% PP	% PS	% ER	% ABS	% SBR
MS-WP-20A	30	65	5		
20B	30	60	10		
20C*	15	65	20		
MS-WP-22A	15		5	80	
22B*	10		30	60	
MS-WP-23A	10	40	10	40	
23B*	10	40	25	30	
23C*	5	40	25	30	
MS-WP-28A*	20	60	10		10
28B*	25	55	10		10

*Could not be melt spun

Table 5 - Fibers for Weak Acid Exchange

Code No.	% PP	% EMA	% PS	% ABS	% NBR	% PAA	% GMA	% SMA-1	% SMA-2	% PMM	% PAAS
MS-WP-11A*	75					25					
11B*	25					75					
11C*	60					40					
11D*	90					10					
MS-WP-18A*	80	10				10					
18B*	70	20				10					
18C*	30	30				40					
18D*		80				20					
MS-WP-18AA*	80	10									10
18CC*	30	30									40
MS-WP-27A*	90						10				
27B*	80						20				
MS-WP-35A*	40							60			
35B*	20							80			
MS-WP-36A*	20		10					70			
36B*	30		15					55			
MS-WP-37A*	20			10				70			
37B*	10			30				60			
MS-WP-38A*	16.7	16.7		8.3					58.3		
MS-WP-42A*		45			5			50			
MS-WP-47A*		60				20		20			
MS-WP-41A		45			5					50	
MS-WP-46A*		30								70	

*Could not be melt spun

Table 6 Vinylpyridine Mixtures

Code No.	% PP	% NPA	% EMA	% PS	% ABS	% PVP	% PVP-HAC	% SVP	% ZnO	% ER
MS-WP-1A*	80					20				
1B*	60					40				
1C*	40					60				
1D	20					80				
MS-WP-2A		75				25				
2B		25				75				
MS-WP-3A*	50		25			25				
MS-WP-4A	30			10		60				
4B	15			5		80				
4C	27.5			2.5		70				
4D*	37.5			2.5		60				
MS-WP-5A*	50						50			
MS-WP-6A	20							80		
MS-WP-12A	25				5	70				
12B	30				10	60				
12C	25				15	60				
12D	25				25	50				
12E	15				5	80				
MS-WP-13A*	30					60		10		
13B*	30					50		20		
MS-WP-14A*	15			5		75			5	
14B*	15			5		60			20	
MS-WP-15A*	15			5		77.5				2.5

*Could not be melt spun

Table 7

Polyethyleneimine and Miscellaneous Mixtures

Code No.	% PP	% EMA	% PS	% ABS	% PVP	% PEI	% SDM	% PAS
MS-WP-16A*	70		10			20		
MS-WP-17A*	70			10		20		
MS-WP-19A*	80	10				10		
19B*	50	25				25		
19C*		80				20		
MS-WP-44A	15			5	70	10		
44B	20			10	60	10		
44C	15			5	60	20		
44D	15			5	50	30		
44E*	20			10	40	30		
RF-PB-129D	40						60	
MS-WP-9A*	75							25
9B*	25							75
MS-WP-10A*	20		5					75

*Could not be melt spun

Table 8

Physical Properties - Cation Exchange Fibers

Code No.	Draw Ratio	8 Filament Denier	Percent Elongation	Tenacity (g/denier)
MS-WP-0A		537	803	0.72
0B		463	-	0.59
0C		549	-	0.49
0D		531	-	0.50
MS-WP-8A		560	-	0.47
8B		687	-	0.48
8B	2:1	351	53	1.10
8C		753	-	0.41
8D		573	-	0.48
8D	3:1	200	43	1.31
8E		602	-	0.50
8E	6:1	96	55	2.49
8F		684	-	
8F	3:1	228	39	1.08
MS-WP-21		711	-	0.53
MS-WP-26C		639	-	-
26C	1.7:1	381	-	0.27
MS-WP-31B		1794	-	0.18
31B	4:1	443	52	1.34
31C		664	-	0.32
31D		687	-	0.51
MS-WP-33A		714	-	0.33
33B		524	-	0.36
33B	2:1	270	50	0.98
MS-WP-34B		1130	-	0.20
MS-WP-48A		733	-	0.23
48B		797	-	0.28
48C		972	-	0.24
48C	3:1	330	38	0.99
48C	4:1	238	27	1.01
MS-WP-40B		717	-	0.34
40B	4:1	168	54	1.14
40B(2)	3:1	248	38	1.79
MS-WP-20A		523	-	0.46
20A	1.2:1	444	103	0.46
20A	3.5:1	150	87	1.33
20A	6:1	85	43	2.34
20B		543	-	0.44
MS-WP-41A		535	-	0.23

Table 9

Physical Properties - Anion Exchange Fibers

Code No.	Draw Ratio	8 Filament Denier	Percent Elongation	Tenacity (g/denier)
MS-WP-1D		484	-	0.39
MS-WP-2A		650	298	0.69
2B		618	-	0.84
MS-WP-4A		589	-	0.70
4B		723	-	0.64
4C		848	-	0.43
MS-WP-6A		597	-	0.56
MS-WP-12A		762	-	0.39
12C		624	-	0.61
12D		842	-	0.36
12E		662	-	0.60
12E	2:1	355	-	0.89
MS-WP-44A		869	-	0.38
44A	1.6:1	545	-	0.48
44A	1.8:1	468	-	0.50
44B		740	-	0.32
44B	1.6:1	447	-	0.55
44C		889	-	0.25
44D		1839	-	0.16
44D	2.3:1	789	-	0.48

the expectation of obtaining good physical properties together with high ion exchange capacity. It is a compromise between MS-WP-8C, which has a high loading of PS and ABS but forms a brittle fiber, and mixtures MS-WP-8B and -8D which have good physical properties but lower ion exchange potential. MS-WP-8E with its 2.49 g/denier tenacity was the strongest fiber obtained in this work. Because of the effectiveness of acrylonitrile-butadiene-styrene (ABS) in preventing loss of sulfonated polystyrene, even without any crosslinking after spinning, attempts were made to spin higher proportions of this material with polypropylene (MS-WP-8F and -8G); and, in fact, it was found that ABS could be spun by itself (MS-WP-21).

Another approach for the incorporation of butadiene in the fiber mixtures is the addition of a copolymer which is high in butadiene. Such is the case with MS-WP-26A to -26I where SBR (25% styrene, 75% butadiene copolymer) is combined with polystyrene and polypropylene. The use of SBR allows higher butadiene and styrene content and a minimum of inert material. However, the fiber obtained from SBR mixtures is usually extremely weak. For example, the tenacity of MS-WP-26C was too low to be measured by the Instron test, and the tenacity of the drawn fiber was only 0.27 g/denier.

Physical properties were greatly improved by spinning SBR with ABS (instead of PS and PP). Thus, MS-WP-31B is strong, 1.34 g/denier, and contains high proportions of styrene and butadiene (see Table 3). Combinations of PP, PS, ABS, and SBR as in Ms-WP-33A and -33B resulted in no substantial improvement in physical properties.

Further refinements in fiber properties were obtained by the use of NBR (15% acrylonitrile, 85% butadiene copolymer). The NBR, having greater high temperature viscosity than the SBR used, was easier to spin. In the series MS-WP034A to -34D, NBR was combined with ABS to give fibers with high butadiene content. MS-WP-34B had the highest butadiene content, 18.7%, and still had good tenacity, 0.98 g/denier. The series MS-WP-48A to -48C was an attempt to improve physical properties while maintaining high butadiene content. Although these mixtures had improved spinning properties, there was little improvement in the fiber tenacity. On the other hand, mixture MS-WP-40B, combining polypropylene, polystyrene, and NBR yielded a much stronger fiber, 1.79 g/denier, while maintaining reasonably high styrene and butadiene content.

Mixture MS-WP-49A is the same as -40B except that the polystyrene was replaced with polymethylstyrene (PMS). This substitution has potential advantage in that the formation of sulfone bridges during sulfonation is more prevalent in PMS (12). The PMS used in this mixture was unsuitable for spinning with PP and NBR because of its low melting point.

As a general rule the difficulty in spinning fibers increased with the butadiene content partly because of instability of the mixtures toward hot working and partly because of poor fiber forming properties of the butadiene copolymers. Although improvement in spinning behavior was

seen by decreasing the mixing time prior to spinning (for example, compare 40B with 40B(2) in Table 8), the effectiveness of crosslinking appeared to be enhanced by thorough mixing. It is reasonable to assume that the most efficient crosslinking which can be achieved by a given amount of butadiene will come from a styrene-butadiene copolymer rather than a blend of polystyrene and polybutadiene. For this reason styrene-butadiene copolymers were specially made for mixtures MS-WP-7A, -29A, -29B, -30A, -32A, -45A. These copolymers ranged from 72% styrene, 28% butadiene to 90% styrene, 10% butadiene. None of the mixtures could be spun. MS-WP-7A showed evidence of being partially crosslinked as the mixture caused very high extruder pressures. Neither SB-1 (90% styrene, 10% butadiene) nor SB-2 (80% styrene, 20% butadiene) could be spun because of thermal instability. The addition of stabilizer in MS-WP-45A did not noticeably improve the spinning properties of SB-2. Low molecular weight and perhaps residual monomer contributed to the instability of SB-1 and SB-2 which decomposed below 200°C. Furthermore, even though the polymerization was taken only to 85% conversion, there was evidence of excessive branching. Nevertheless, copolymers of this type should ultimately lead to improved sulfonic acid ion exchange fibers.

Mixtures Containing Epoxy Resins

Epoxy resins (ER) provide another promising method for crosslinking in fibers containing sulfonated polystyrene. The epoxy resin can be crosslinked with amines, peroxide, or possibly sulfuric acid itself. Moreover, the phenyl groups in the ER can be sulfonated, thus minimizing the loss in capacity due to the crosslinking agent. The miscibility of ER with PP-PS or PP-ABS mixtures is limited to about 10% ER (see Table 4). Attempts to include both epoxy resin and SBR with PP-PS (MS-WP-28A and -28B) were unsuccessful. However, the ability to spin such mixtures is extremely sensitive to variations in the control of the spinning extruder as well as thermal history of the mixture. The principal difficulty in spinning epoxy resin was due to its low viscosity at typical PP-PS melt temperatures; thus, higher molecular weight ER is necessary for better results.

Mixtures for Weak Acid Cation Exchangers

As shown in Table 5, many attempts were made to spin weak acids and anhydrides for use as weak cation exchangers. None of the mixtures could be melt spun. Polyacrylic acid (PAA) could not be spun with either PP or EMA (sodium salt of ethylene-methacrylic acid copolymer) nor could the sodium salt of PAA be spun with these materials. The problems in melt spinning mixtures containing PAA were probably the ionic character of the acid and the possibility of crosslinking through formation of the acid anhydride. The mixtures containing PAA which showed the best spinning behavior, MS-WP-18A and -18B, were prepared for spinning by mixing the PAA (25% aqueous solution) with powdered PP before dehydration, thus decreasing the chances of crosslinking via acid anhydride formation.

As an alternative to the ionic PAA, the spinning of several maleic anhydride copolymers was attempted with the aim of hydrolyzing the anhydride after spinning. GMA (copolymer of methyl vinyl ether and maleic anhydride) could not be spun with PP because of its decomposition at ordinary PP melt temperatures. Both the 1:1 and 2:1 copolymers of styrene and maleic anhydride (SMA-1 and SMA-2) were tested for compatibility with PP or EMA. None of these mixtures could be spun, but the 2:1 (styrene:maleic anhydride) copolymer had better extruding behavior. Although the SMA copolymers are fiber forming, the fiber pulverizes with a small amount of flex or compression, extruded filaments from the SMA mixtures in Table 5 had physical properties similar to pure SMA.

The only successful approach to making a weak acid cation exchanger was the mixture MS-WP-41A containing PMM (methyl methacrylate-styrene-butadiene blend). After spinning, the methyl methacrylate can be hydrolyzed to give methacrylic acid. The fiber (MS-WP-41A) was quite weak with only 50% PMM, but increased PMM content and increased strength will undoubtedly be possible.

Anion Exchange Fibers Containing SDM

The anion exchange fibers had two basic types of active ingredients - polyvinylpyridines and polyamines. In previous work (13) it was demonstrated that SDM (styrene-dimethylaminopropyl maleimide copolymer) could be cospun with PP in the ratio 60% SDM, 40% PP. This fiber, RF-PB-129D, has excellent physical properties and can be crosslinked with dibromoalkanes; but because of the high equivalent weight of SDM (286 gequiv), the maximum calculated ion exchange capacity, 2 meq/g, is low. Therefore, attempts were made to spin fiber with PVP (1:1 copolymer of 2-vinylpyridine and 2-methyl-5-vinylpyridine) whose equivalent weith is 112 g/equiv, about 40% that of SDM.

Vinylpyridine Anion Exchange Fibers

PVP and PP mixtures are compatible for spinning only in the extremes of very low concentration of PVP or high concentrations, about 80% PVP or greater (see Table 6). In the latter case the fibers are quite weak. PVP neutralized with acetic acid (MS_WP-5A) was equally incompatible with polypropylene. Polystyrene has a marked effect on the ability to spin PVP with polypropylene. Although the 4:6 PP-PVP mixture (MS-WP-1C) could not be spun, the mixture MS-WP-4A (3:1:6 PP-PS-PVP) gave a fiber of good appearance, fair tensile strength, and slight cold draw capability. As little as 5% polystyrene gave excellent physical properties to the fibers. With 2.5% PS (MS-WP-4C and -4D) the fibers were quite weak and could not be drawn. Mixtures with ABS in the place of PS (MS-WP-12A to -12E) were more easily spun and of comparable strength. None of the mixtures with PS could be drawn; but one fiber with ABS, MS-WP-12E, was drawn to improve the strength.

Nylon 6 and PVP are compatible for spinning over a wide range of concentrations (MS-WP-2A and-2B). Fiber MS_WP-2B has good tenacity but no

appreciable elongation at break; the fiber could not be drawn. EMA, which is a compatibilizer for SDM and PP, does not aid in the spinning of PVP and PP as shown by mixture MS-WP-3A.

Since polystyrene is a compatibilizer for PVP and PP, one might expect a styrene-vinylpyridine copolymer (SVP) to be compatible with PP. Such is the case with MS-WP-6A. This fiber, however, is not particularly superior to those with PVP and has the disadvantage of a high monomer equivalent weight compared with PVP. If, on the other hand, SVP is used in small amounts in an effort to make PP and PVP compatible (that is, in the same capacity as PS or ABS in MS-WP-4A to 4D or MS-WP-12A to 12E), the mixtures cannot be spun. Thus, MS-WP-13B, which had the same polypropylene, styrene, and vinylpyridine concentrations as MS-WP-4A but in different polymer form, could not be spun.

In the compounding of polyamines with elastomers, zinc oxide is found to have a curing effect on the polyamines. Thus, it is plausible that ZnO might provide crosslinking in PVP and other polymeric amines used for ion exchange fibers. The mixture MS-WP-14A containing 5% ZnO behaves as a crosslinked material when extruded (manifested by a high pressure on the extruder die), but the extruded material swells rapidly and loses PVP in acidic solution. Based on these experiments it is unlikely that ZnO can be useful in the prevention of PVP extraction.

Since it is known that PVP is a cure for epoxy resin, the effect of adding a small amount of ER to PP-PS-PVP mixtures was investigated. The mixture MS-WP-15A with 2.5% ER had excessive crosslinking and could not be spun. It appears that in order to have a spinnable mixture the degree of crosslinking must be so low as to be practically negligible, and therefore, all crosslinking must be effected after spinning.

Mixtures Containing Polyethyleneimine

Polyethyleneimine (PEI) is not compatible for spinning with PP. In mixtures MS-WP-16A and -17A (Table 7) it was found that unlike the case with PVP neither PS nor ABS improved the spinning characteristics of PP and PEI. Furthermore, the series MS-WP-19A to -19C showed that EMA is not compatible with PEI nor does it compatibilize PP and PEI. As seen by mixtures MS-WP-44A to -44E, PEI is compatible with PVP or at least is compatible with a PP-ABS-PVP mixture. It would appear then that a four component system is necessary for spinning PEI along with PP; that is, compatibility of PEI requires PVP which is in turn compatibilized with PP by ABS. The substitution of PEI for PVP should lead to higher capacities since the PEI equivalent weight is only about 35% that of PVP. Up to 30% PEI has been spun with PP, ABS, and PVP; this fiber, MS-WP-44D, has a maximum calculated amine content of 12 meq/g.

Miscellaneous Fiber Mixtures and Treatments

The polyaminostyrene (PAS) - polypropylene mixtures could not be extruded (MS-WP-9A, -9B, -10A). The polyaminostyrene was likely impure or crosslinked since it caused very high pressures at the extruder die.

Fibers for which crosslinking was attempted by irradiation are listed in Table 10 along with dosages. The effect of the irradiation on the anion exchange fibers was too small to be useful. Likewise none of the fibers containing polystyrene were appreciably crosslinked. Crosslinking via irradiation probably has little merit for polypropylene-polystyrene mixtures as in most of the fibers in Table 10. This is due to the fact that sufficient irradiation to crosslink the polystyrene at the same time seriously degrades the polypropylene.

Table 10

Irradiation of Fibers

	Dosage (watt-hour)			
Sample No.	8	16	24	32
MS-WP-2B	x	-	x	-
MS-WP-4B	x	x	-	-
MS-WP-OB	x	x	-	-
MS-WP-OC	x	-	x	-
MS-WP-OD	x	-	x	-
MS-WP-8B	x	x	x	x
MS-WP-8C	x	x	-	-
MS-WP-8D	x	x	x	x

x indicates irradiated samples

EVALUATION OF CATION EXCHANGE FIBERS

Sulfonic Acid Exchangers

Studies of the sulfonation of polystyrene and polypropylene-polystyrene fibers indicated that although a crosslinking agent is definitely needed for such fibers, polypropylene itself holds some of the sulfonated polystyrene in the fiber. Samples of MS-WP-OB (1:1 PP-PS) were sulfonated using (1) concentrated sulfuric acid, (2) fuming sulfuric acid (30% SO_3) and (3) chlorosulfonic acid. Concentrated sulfuric acid was ineffective in producing a high degree of sulfonation in the fiber; the maximum capacity obtained was 0.5 meq/g (dry fiber in the acid form). Hot sulfuric acid gave some crosslinking but the loss of polystyrene sulfonic acid was faster than the rate of crosslinking. The action of fuming sulfuric acid on the fiber permitted a higher degree of sulfonation, but with increasing sulfonation there was a corresponding loss of weight in the fiber due to increased water solubility of the sulfonated polystyrene. Moreover, several regenerations brought marked decrease in

the total capacity of the fibers treated with fuming sulfuric acid. The highest degree of sulfonation in the fiber, 3.0 meq/g, was achieved with chlorosulfonic acid. The capacity was unchanged after three regenerations indicating that some crosslinking had taken place. In separate experiments polypropylene fiber samples were treated with fuming sulfuric and chlorosulfonic acids. In neither case was sulfonation of the polypropylene fiber detected. Thus, it is calculated that the fiber described above having a capacity of 3.0 meq/g has 78% of its aromatic rings sulfonated. Since 10% sulfonation would render the polymer water soluble, the chlorosulfonic acid treatment must have caused sufficient crosslinking to maintain the 3 meq/g capacity. Presumably the crosslinking is accomplished by means of -S- or $-SO_2-$ bonding. Subsequent experiments showed that this type of crosslinkage is not very stable to prolonged exposure to aqueous solution.

The sulfonation of MS-WP-OC and OD (80% PS and 90% PS, respectively) resulted in capacities up to 4 meq/g. For these samples the crosslinking afforded by chlorosulfonic acid sulfonation was clearly inadequate. Swelling of the fiber was excessive; and after several hours in solution, a significant amount of the sulfonic acid was leached from the fiber. The presence of peroxidized polypropylene in MS-WP-OC did not result in a noticeable increase in crosslinking.

The substitution of acrylonitrile-butadiene-styrene for part or all of the polystyrene reduced the loss of styrene sulfonic acid from the fiber even without any special efforts to crosslink the butadiene. Samples of MS-WP-8A, -8B, -8C, and -8D were sulfonated with chlorosulfonic acid for two minutes. After rinsing, the ion exchange capacity was determined and the fiber was regenerated. Four cycles of titration and regeneration are shown in Table 11. The "capacities" are listed in terms of meq of acid

Table 11

Effect of Titration-Regeneration Cycles on the Capacity

No. of Cycles	MS-WP-8A meq acid	MS-WP-8B meq acid	MS-WP-8C meq acid	MS-WP-8D meq acid
1	5.91	6.60	9.46	5.12
2	4.53	5.03	7.78	4.73
3	4.13	4.74	6.80	4.20
4	4.11	4.49	6.42	4.06
Sample weight after cycle No. 4 (g)	1.455	1.920	2.124	1.555

titrated rather than meq/g because the samples were dried and weighed only after the fourth regeneration. The apparent decrease in capacity is almost certainly accompanied by a decrease in sample weight due to the loss of highly sulfonated polystyrene. Thus, the change in total

capacity expressed in meq/g is smaller than the change in meq acid titrated. However, since in the evaluation of ion exchange performance the sample weight for the final cycle determines the maximum capacity for succeeding cycles, an "apparent capacity" defined as the meq of acid titrated divided by the sample weight during the final cycle may be used to describe the change in sample performance with the number of titration-regeneration cycles. This is shown in Figure 1 which is essentially a plot of the data of Table 11 normalized so that the ordinate for the final titration is the true total capacity of the fiber in meq/g. With regard to swelling, the fibers having more ABS have less swelling.

A more extensive study of the change in capacity with cycles of exhaustion and regeneration is shown in Figure 2. The sample, MS-WP-8D (3:1 draw), was sulfonated with $H_2SO_4 \cdot 15\%\ SO_3$, and its total capacity was followed through 25 titration-regeneration cycles. The sample was dried and weighed only after the twentieth cycle; all the capacities of Figure 2 are calculated on the basis of that weight. The scatter in the data (probably due mostly to variations in the degree of regeneration) does not permit establishment of a definite trend in the total capacity. From the second through the twentieth cycle, there is no change in total capacity within experimental error, but the five cycles subsequent to drying indicate a loss of capacity. The average capacity of the sample through 20 cycles (excluding the first) was 2.91 meq/g dry fiber. After the 25 cycles there was no visible deterioration of the fiber.

In other sulfonation experiments on the PP-PS-ABS fibers it was found that the total capacity is not simply related to the time of exposure to the sulfonating agent. Rather, the capacity increases with time of sulfonation to a maximum and then decreases. For example, a sample of MS-WP-8D (3:1 draw) sulfonated in $ClSO_3H$ for 2 minutes had a total capacity of 2.5 meq/g whereas another sample of the same fiber exposed to $ClSO_3H$ for 8 minutes had capacity of 2.4 meq/g. The reason for this behavior is the loss of highly sulfonated polystyrene from the fiber which eventually competes with the rate of sulfonation. Therefore, the PP-PS-ABS fibers still have insufficient crosslinking.

Column Elutions of Sulfonic Acid Exchangers

Improved sulfonic acid cation exchanger fiber was obtained from the sulfonation of MS-WP-8F (25% PP, 75% ABS) with $H_2SO_4 \cdot 15\%\ SO_3$. This fiber was finely cut and placed in a buret for evaluation. By elution with excess NaCl and titration of the liberated acid the total capacity was determined to be 3.16 meq/g dry fiber. The column was regenerated with H_2SO_4 and eluted with 0.004 N NaCl at 6.5 ml/min. The effluent was collected periodically by the emptying of a siphon cup, and the acid content of each fraction of effluent was determined. The breakthrough curve for this elution is shown in Figure 3 where the ratio of effluent to influent concentrations is plotted against the number of siphon cup fills. The volume of effluent emptied from the siphon cup had unexpectedly large variations resulting in a random error for each measurement. However, the error is not cumulative so that the sense of the

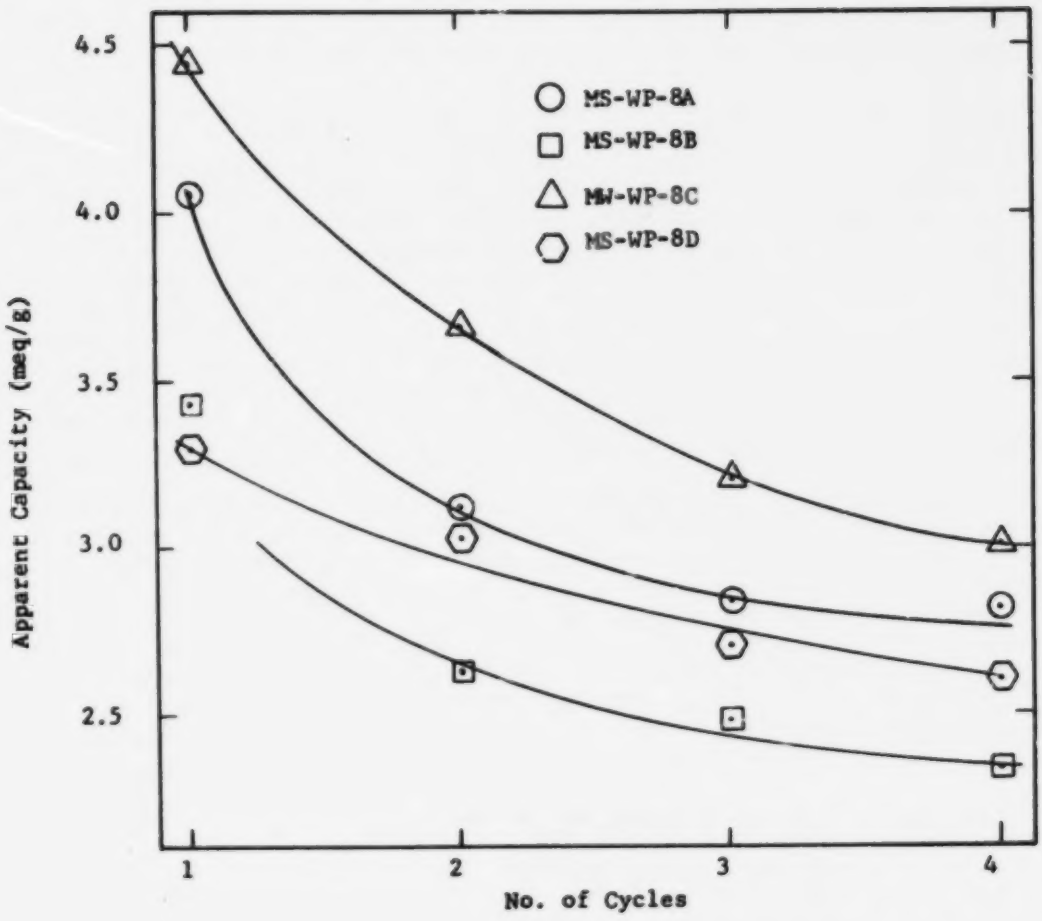

Figure 1

Effect of the Number of Titration-Regeneration Cycles on the Capacity

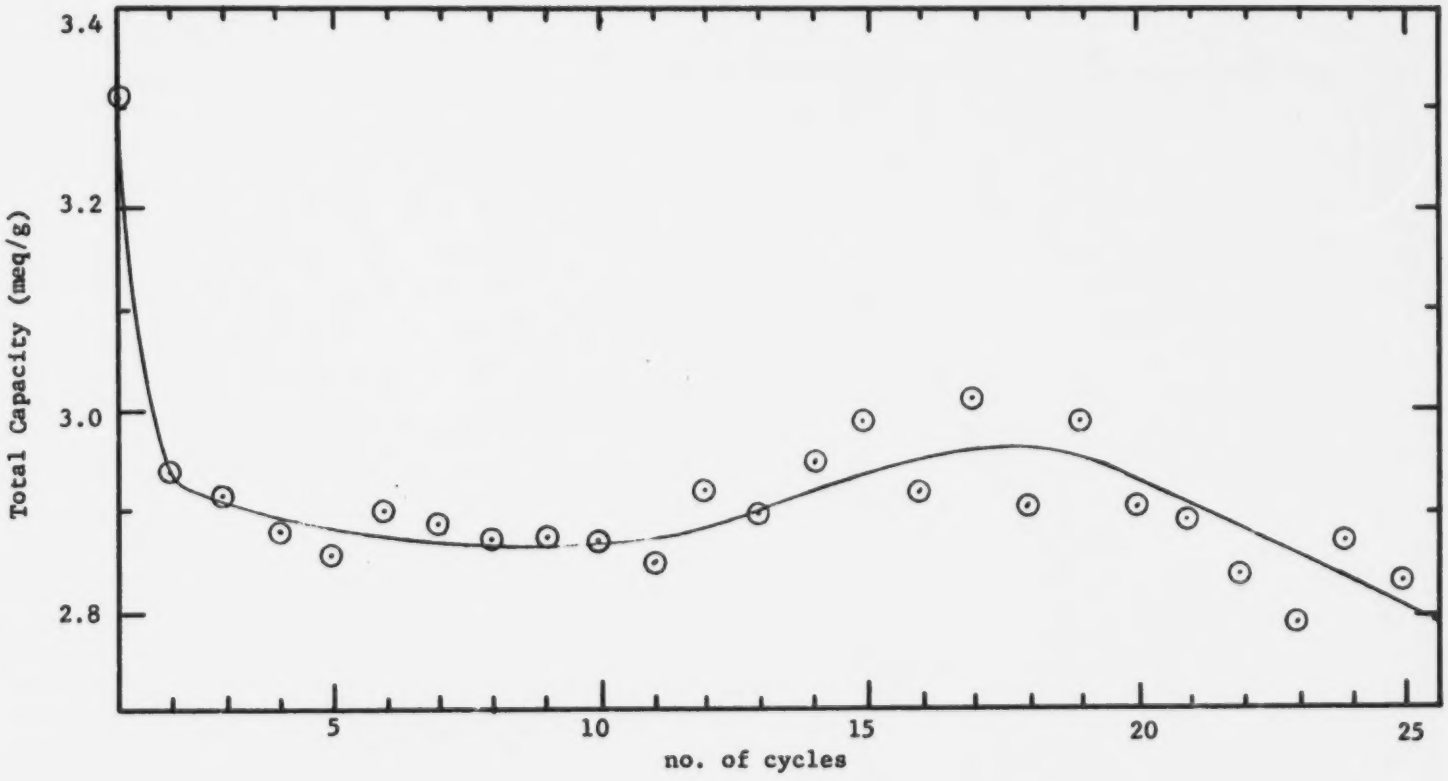

Figure 2

Total Capacity of Sulfonated PP-PS-ABS Fiber

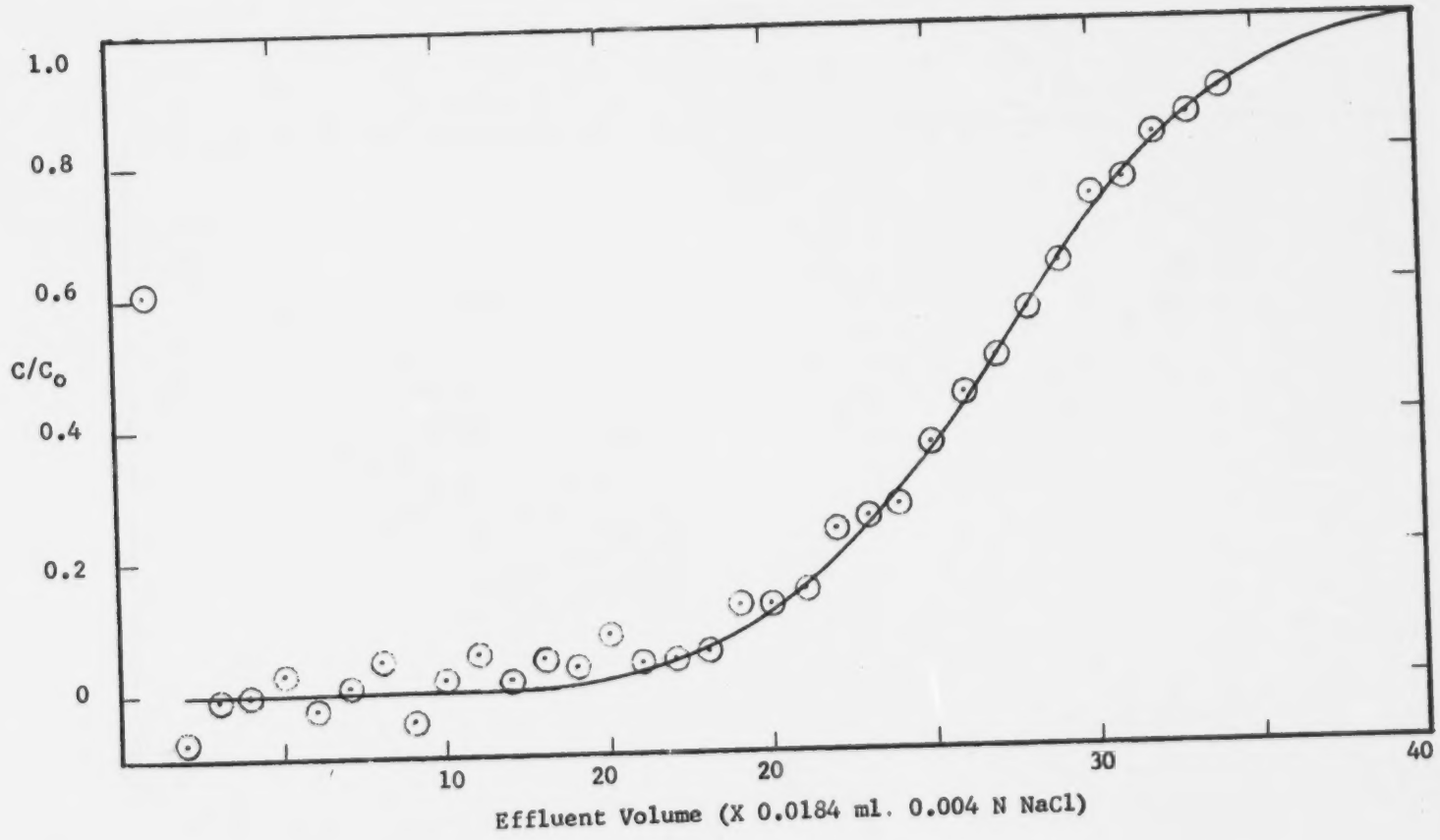

Figure 3

Breakthrough Curve for Sulfonated PP-ABS Fiber (I-141)

curve is accurate; since a total of 1850 mg NaCl solution was passed through the column, the average volume per siphon cup fill was 54 ml. The breakthrough capacity, 1.5 meq/g, was slightly less than half the total capacity under these operating conditions.

Fiber such as MS-WP-8F, which was used for the column evaluation of Figure 3, has enough swelling to seriously degrade its physical properties. In fibers with higher degrees of sulfonation the swelling was correspondingly greater and in some cases sufficient to cause hydraulic problems in column operation. In fiber containing epoxy resin (for example, MS-WP-23A) swelling was reduced by curing the epoxy with diamines prior to sulfonation. The sulfonation process alone did not give appreciable crosslinking.

Further improvements in crosslinking were obtained with fiber MS-WP-26A (20% PP, 70% PS, 10% SBR) by treatment with t-butyl peroxide. The crosslinking afforded by this procedure greatly reduces the swelling of the sulfonated fiber in comparison with the uncured sulfonated fiber. Sulfonation of the cured fibers with funing sulfuric acid gave total capacities up to 4.0 meq/g. However, during the sulfonations the loss of sulfonated polystyrene was evident and the total capacities decreased by several percent after the first cycle of titration and regeneration.

In contrast with MS-WP-26A, the peroxide curing of MS-WP-21 (ABS fiber) was much more effective even though the butadiene content was about the same in both fibers. Very little sulfonated polystyrene was lost during the sulfonation and the swelling of the ABS was less than that of MS-WP-26A. A finely cut sample (2 g) of cured and sulfonated ABS fiber was placed in a column and eluted with 0.05 N $CaCl_2$. The results of three elutions at various flow rates are given in Figure 4. Total capacities were obtained from the area above the breakthrough curves. By way of comparison the same solution was passed through a sample of equal weight of commercial resin (Rohm & Haas IR-120) in an identical column. One such elution is shown in Figure 5. The total capacity of the fiber was 4.2 meq/g compared with 4.6 meq/g for the resin beads. On the other hand, the breakthrough capacity of the fiber at 8.4 ml/min was 3.8 meq/g compared with 1.3 meq/g for the beads at a flow rate of 6.0 ml/min. An even greater difference between the fiber and beads was evident at higher flow rates. At 26.8 ml/min the breakthrough capacity of the fiber was 3.4 meq/g whereas at 32.6 ml/min the breakthrough capacity of the beads was 0.3 meq/g. The fiber and bead capacities are summarized in Table 12.

Table 12

Breakthrough Capacities for $CaCl_2$ Elutions

ABS Fiber		Rohm & Haas IR-120	
Flow Rate (ml/min)	Breakthrough Capacity (meq/g)	Flow Rate (ml/min)	Breakthrough Capacity (meq/g)
3.4	3.8	2.5	2.9
8.4	3.8	6.0	1.3
26.8	3.4	32.6	0.3

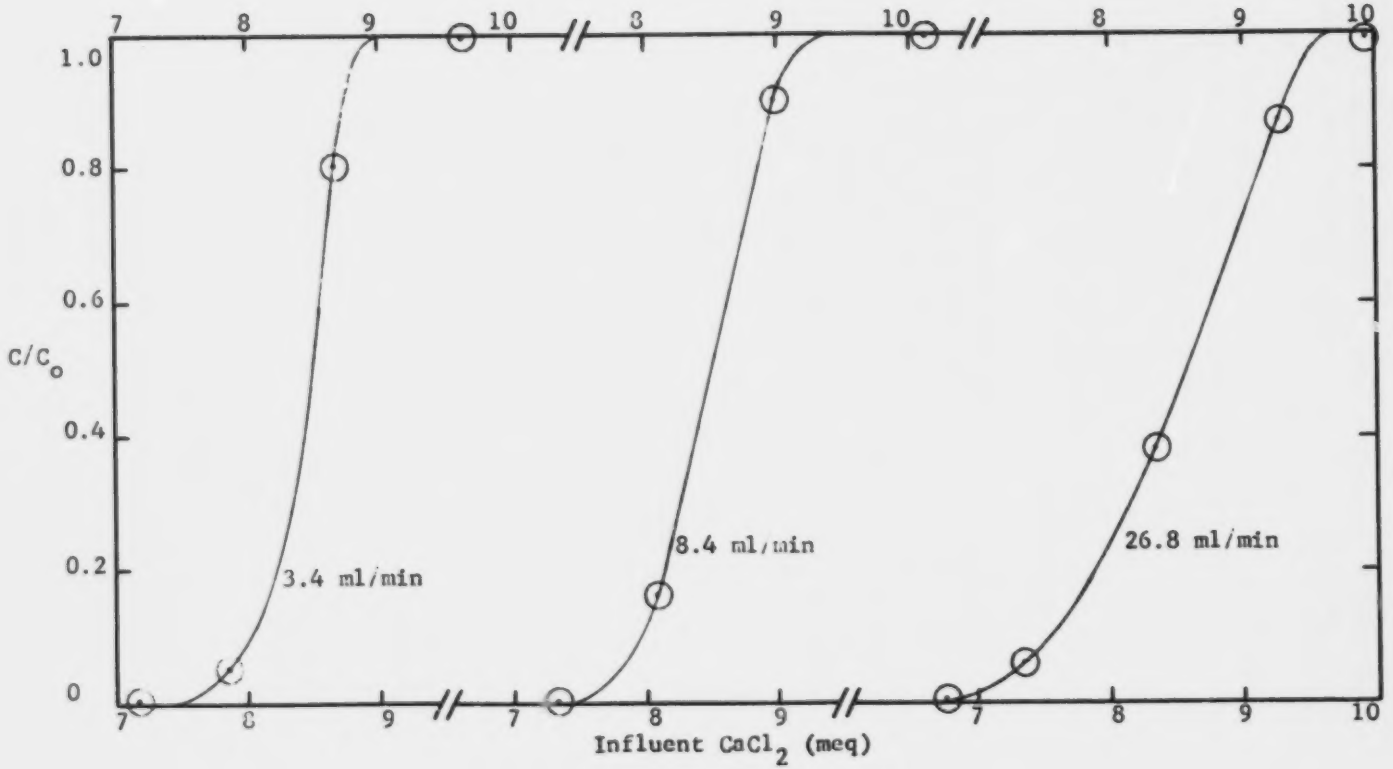

Figure 4

Breakthrough Curves for Sulfonated ABS Fiber (I-177)

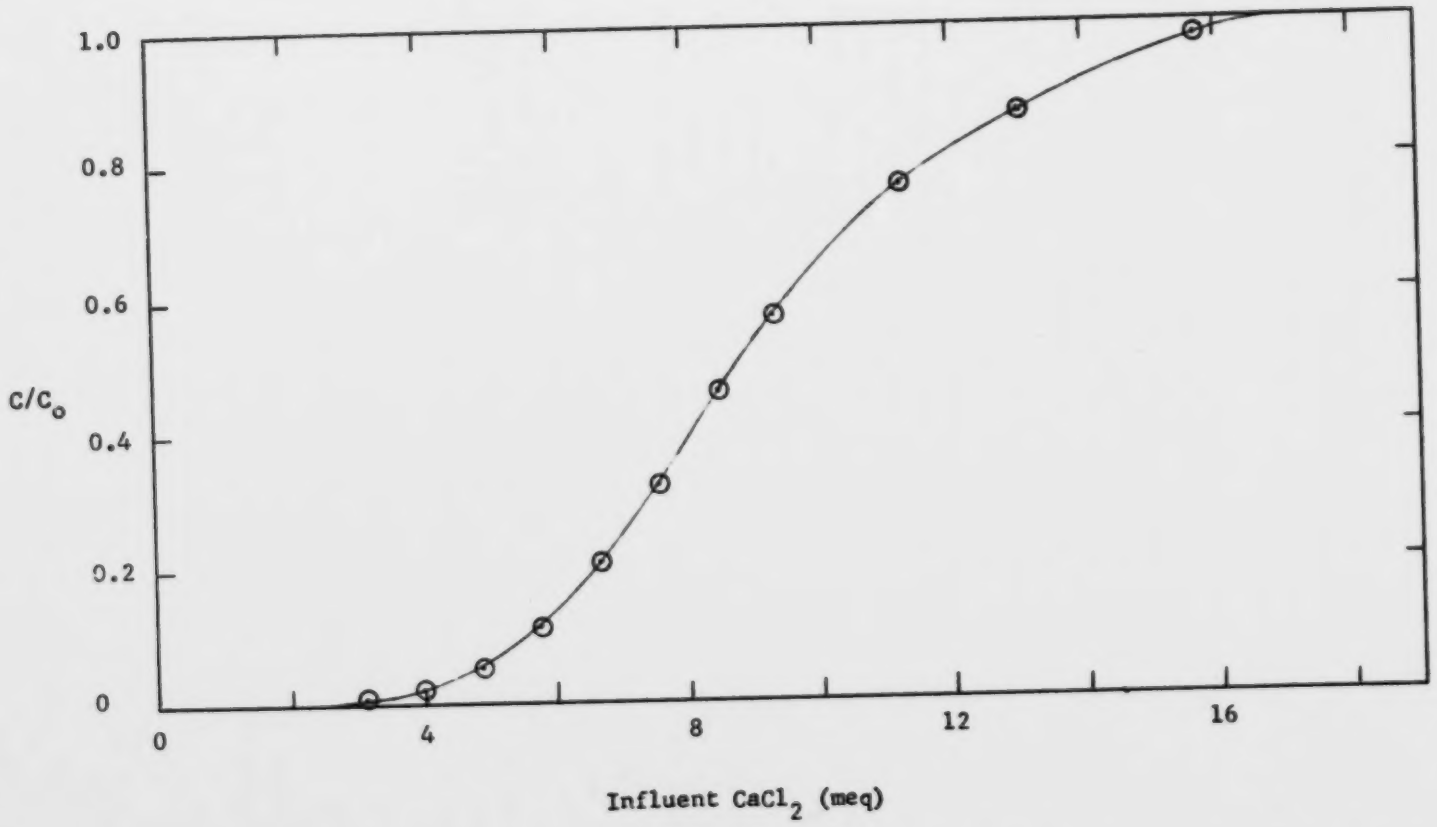

Figure 5

Breakthrough Curve for Rohm & Haas IR-120 Resin

In the case of volume capacities the fiber would not compare so favorably with the commercial resin. The swelling of the fiber was about four times that of the beads which to a large extent accounts for the high ratio of breakthrough to total capacity in the fiber. Nonetheless, these shallow bed elutions indicate the probability of a higher rate of exchange in the fiber.

The most direct approach toward reducing the swelling of the cation exchange fibers in aqueous solution is to increase the butadiene content since the degree of crosslinking obtained in the peroxide or sulfuric acid cures is proportional to the butadiene content (swelling is also reduced by incomplete sulfonation but at the expense of decreased ion exchange capacity). The fiber having the greatest percentage of butadiene was MS-WP-34B with 18.7%. A finely cut sample of this fiber, cured in sulfuric acid and sulfonated with fuming sulfuric acid, occupied a volume of 5 ml per gram of fiber in a column. The column was eluted with 0.02 N $CaCl_2$. The breakthrough curves are shown in Figure 6. In the elution at 3.0 ml/min the breakthrough capacity was 96% of the total capacity, 3.8 meq/g. At the higher rate of 15.3 ml/min the breakthrough capacity was still 92% of the total capacity. The breakthrough capacity of this fiber exceeds that of sulfonated styrene divinylbenzene resin beads (Rohm & Haas IR-120, see Table 12) both on a dry weight and volume basis. However, the swelling of this fiber in aqueous solution still causes undesirable loss in strength and durability. Much of the weakness of this cation exchange fiber can be attributed to the original fiber which was weak and could not be drawn. Therefore, the need for a compromise between high butadiene content and improved fiber strength is evident.

In fiber MS-WP-40B (25% PP, 60% PS, 15% NBR) the butadiene content of 12.8% was less than the 18.7% of MS-WP-34B but the fiber could be drawn to give a tenacity of 1.8 g/denier compared with 0.2 g denier for MS-WP-34B. A sample of this fiber, hand cut to an average length of 3 mm, was cured with sulfuric acid and then divided into four parts for sulfonation with $H_2SO_4 \cdot 7.5\%\ SO_3$ for varying lengths of time. The total capacity is given for each sulfonation time in Table 13. Also listed in

Table 13

Sulfonation of MS-WP-40B

Sulfonation Time (min)	Total Capacity (meq/g)	$\frac{V + \Delta V}{V}$
5	2.75	2.65
10	3.96	4.86
20	4.16	7.18
40	4.19	16.14

Table 13 is the volume swelling factor, $(V + \Delta V)/V$, calculated from changes in diameter on the assumption of negligible swelling in the axial direction. Figure 7 shows the relationship between the swelling factor

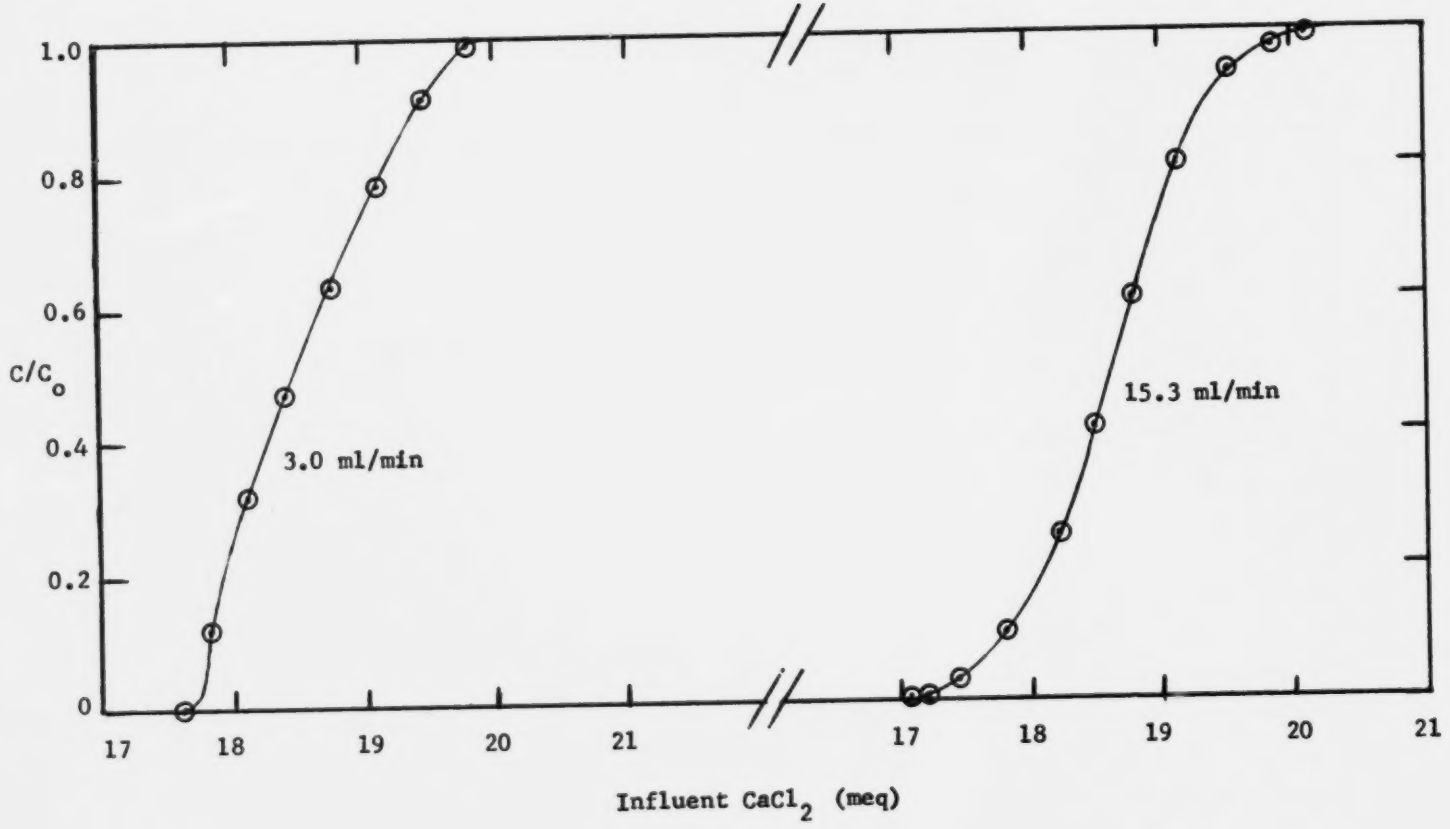

Figure 6

Breakthrough Curves for Cation Exchange Fiber II-9

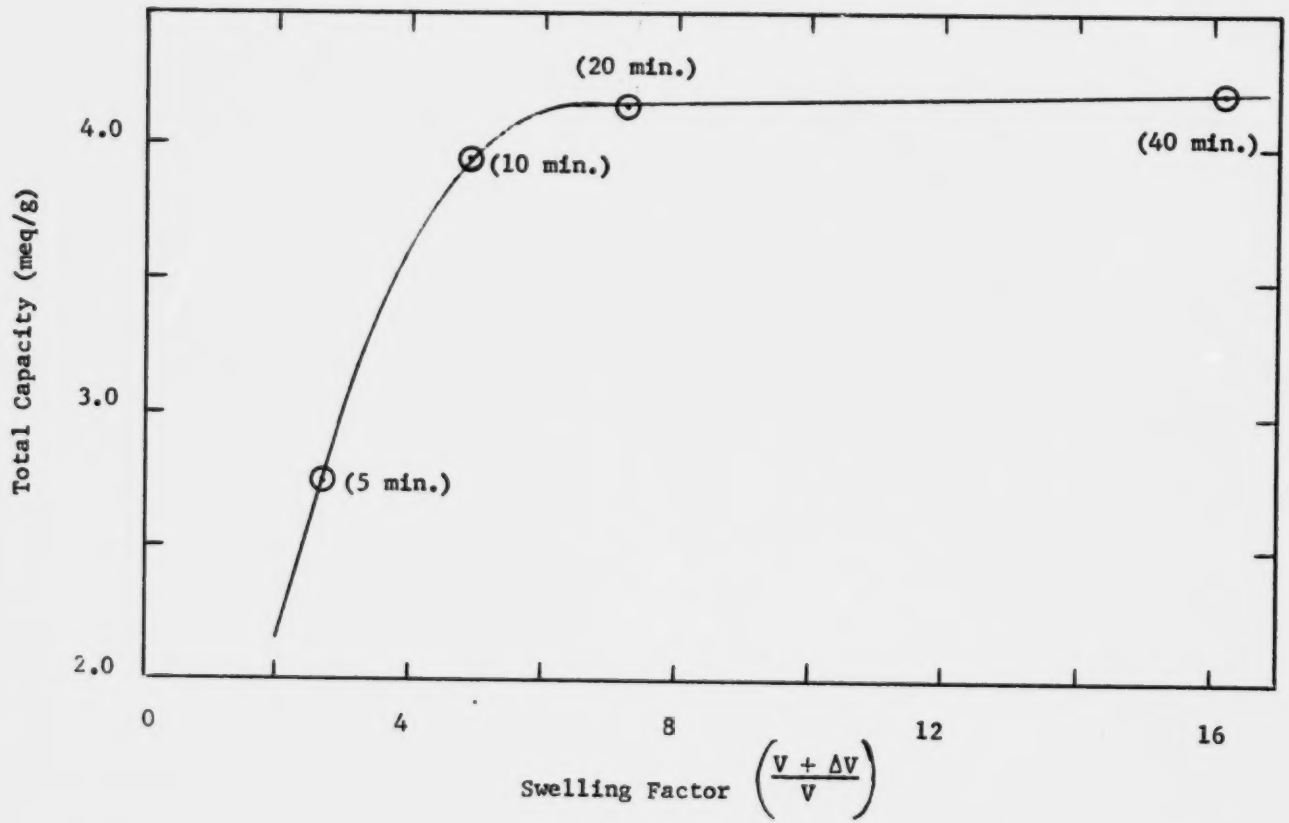

Figure 7

Total Capacity versus Swelling for MS-WP-40B

and the total capacity. The increase in swelling after the leveling of the total capacity is attributed to a loss of highly sulfonated polystyrene while the sulfonation proceeds. It appears that the maximum ion exchange capacity represents a steady state balance between continuing sulfonation and extraction of highly sulfonated polystyrene. Thus, the increase in swelling is related to an increase in degree of sulfonation of the styrene remaining in the fiber. Figure 7 points to the importance of a strictly controlled sulfonation for this type of fiber in order to obtain high capacities with minimum swelling.

Selectivity Coefficients for Sulfonic Acid Exchangers

In accordance with the results of Table 12 a sample of knitted MS-WP-40B was cured with H_2SO_4 and sulfonated with chlorosulfonic acid to a total capacity of 3.5 meq/g. The fabric was then finely cut and placed in a column for evaluation. Breakthrough curves for calcium elutions are shown in Figures 8 and 9. The column was also eluted with a solution containing ammonium ion in addition to calcium ion. Breakthrough curves for calcium and ammonium are given in Figures 10 and 11, respectively. The analysis of ammonium ion in the effluent presented serious reproducibility problems. Although it is difficult to extract quantitative results from Figure 11, some information may be derived by comparison with Figures 8, 9 and 10. It is seen from Figures 8 and 9 that the total capacity of the fiber is fairly constant, i.e., about 8.8 meq; the same capacity is therefore expected for Figure 10. Substracting the calcium absorbed in Figure 10 from the total capacity (assumed to be a maximum of 8.8 meq) of the fiber gives the maximum amount of ammonium ion absorbed in the column, 0.525 meq. This does not agree with the ammonium ion sorption of Figure 11. The difference between the two results is represented graphically by the area enclosed by the square in Figure 11. Clearly, because of the scatter of the data, this area could be accounted for by drawing a different curve - especially between 4.0 and 5.0 meq on the abscissa. The first sample analyzed for ammonium ion was at 4.86 meq NH_4^+, just prior to calcium ion breakthrough. However, it appears that ammonium ion breakthrough may have occurred well before detection of calcium ion breakthrough.

The selectivity coefficient K_B^A may be calculated from the steady state absorptions on the column and influent concentrations. Selectivity coefficients are variously defined in terms of different concentration units. Here we use the molal selectivity coefficient defined as follows:

$$K_B^A = \frac{\bar{m}_A^{|z_B|}}{\bar{m}_B^{|z_A|}} \cdot \frac{m_B^{|z_A|}}{m_A^{|z_B|}}$$

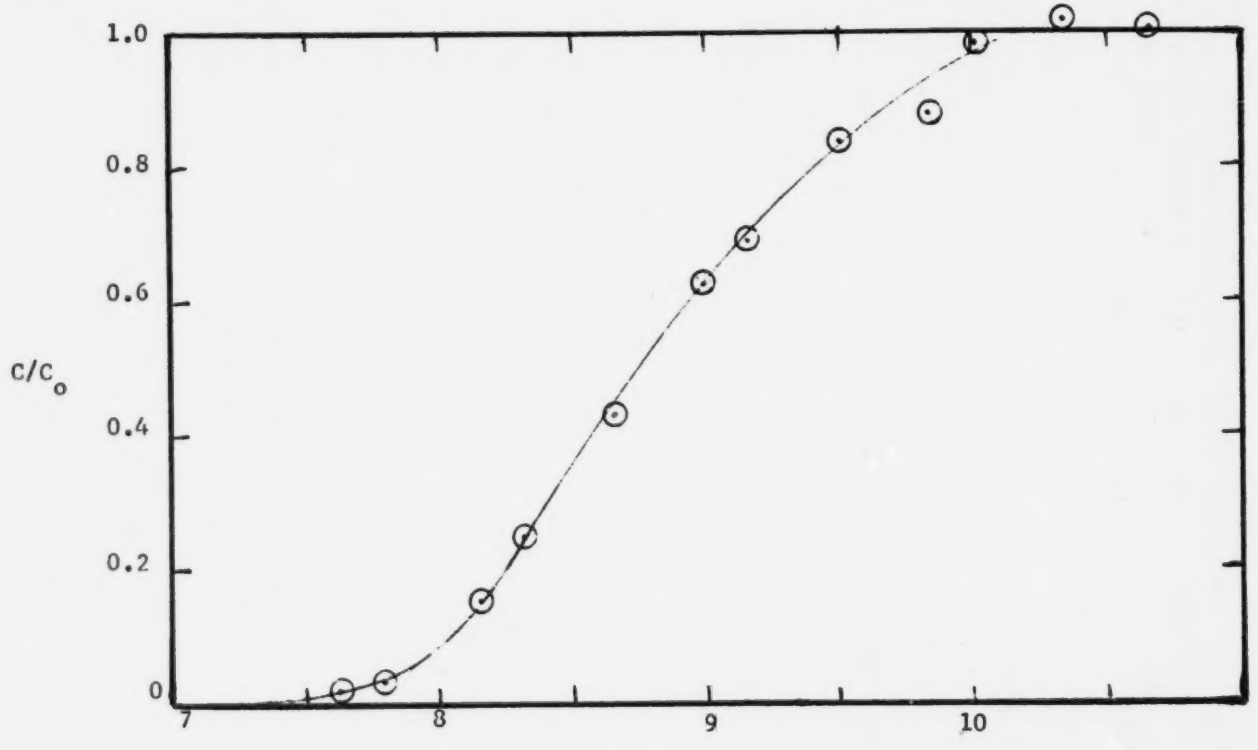

Figure 8

Sulfonated MS-WP-40B, First Elution

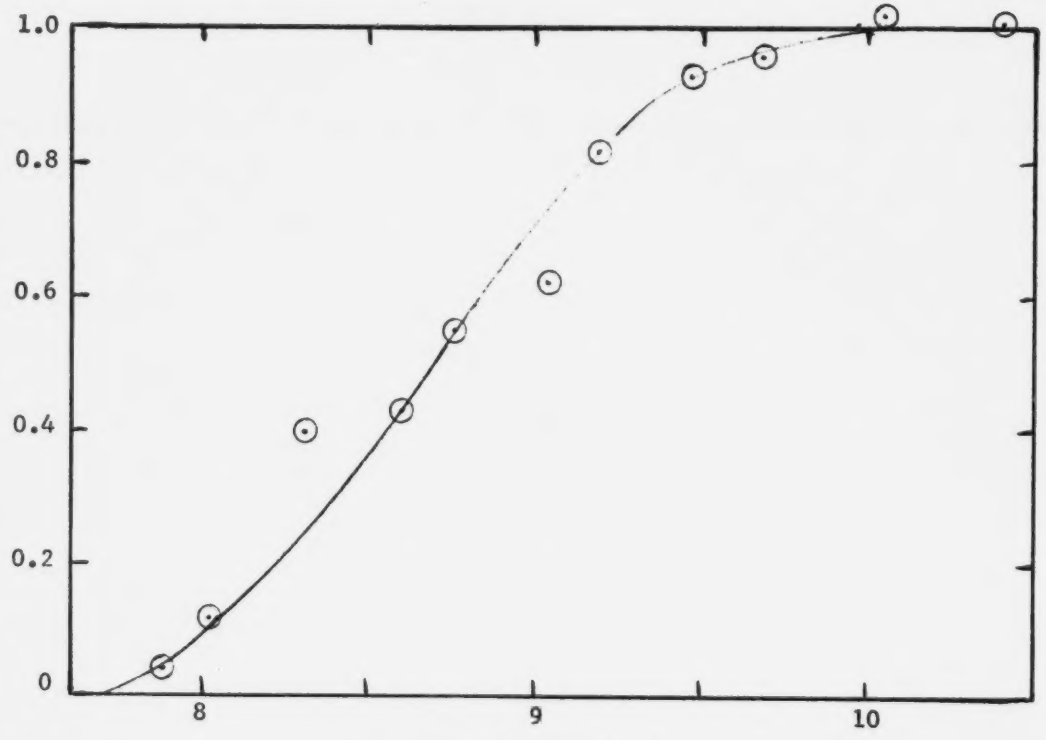

Figure 9

Sulfonated MS-WP-40B, Second Elution

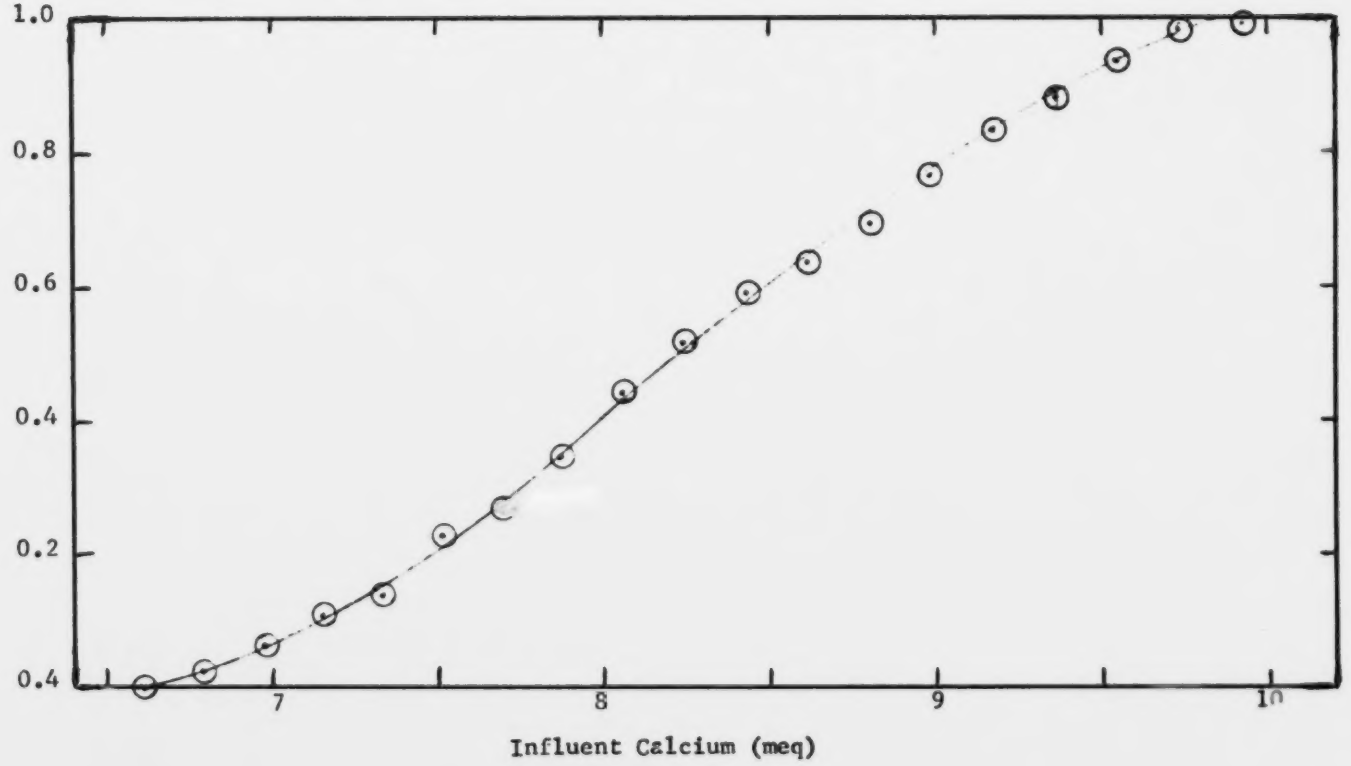

Figure 10

Calcium Ion Breakthrough for Ammonium-Calcium Elution of Sulfonated MS-WP-40B

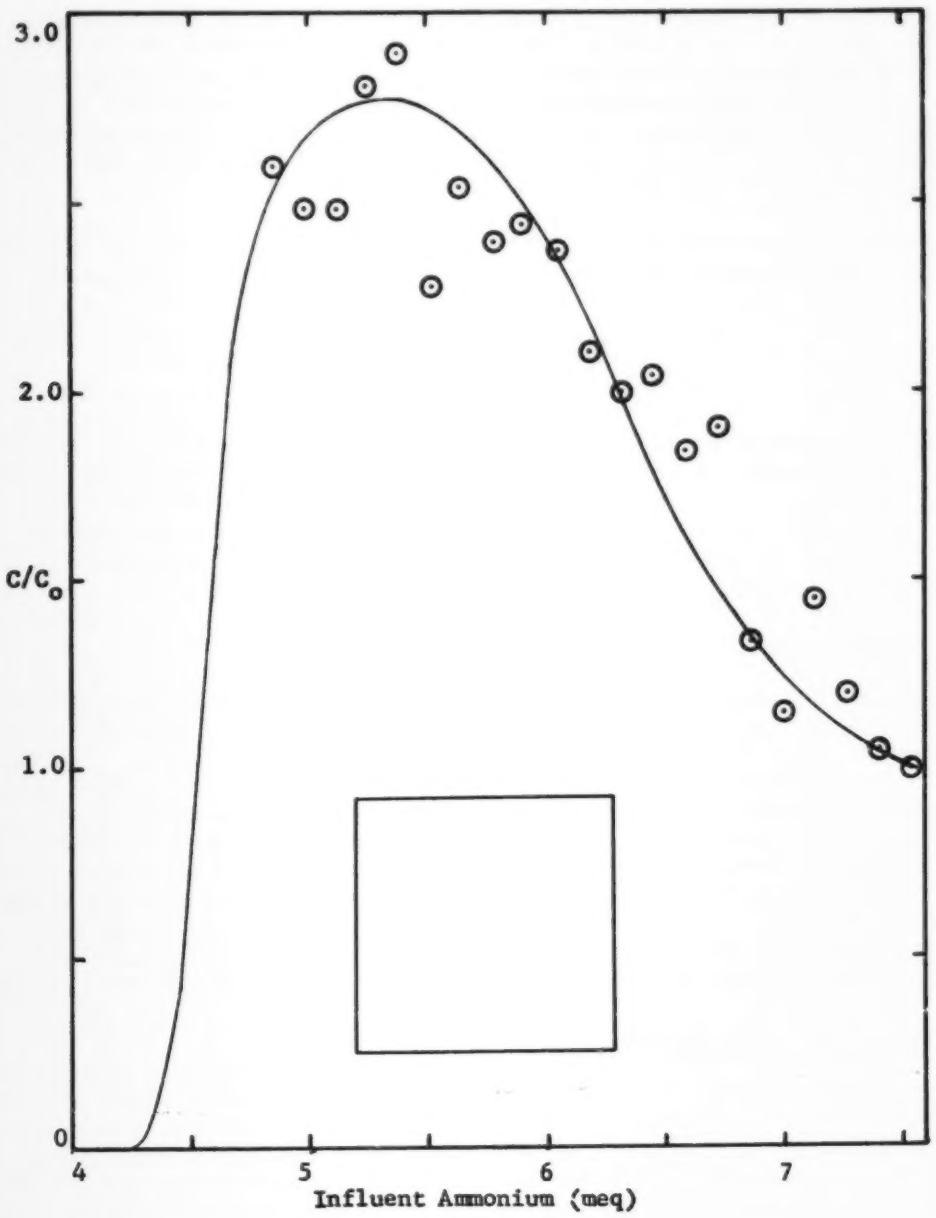

Figure 11

Ammonium Ion Breakthrough for Ammonium-Calcium Elution of Sulfonated MS-WP-40B

where $\bar{m}$ and m are molalities in the absorbed and liquid phase respectively, and z is the valence. The selectivity coefficient as defined above is not an equilibrium constant; the equilibrium constant has the same form as the molal selectivity coefficient but is expressed in terms of activities. Therefore, the selectivity coefficient may be expected to vary with the relative concentrations of A and B and with the total concentration of A and B.

Using the results of Figure 10 and assuming a total capacity of 8.80 meq for the column, the molal selectivity coefficient may be calculated:

$$K_{Ca^{++}}^{NH_4^+} = \frac{(.525)^2}{8.275} \qquad \frac{(.005846)}{(.004243)^2} = 10.8$$

It can be inferred from the above relationship that in the case of solutions having ammonium ion in concentrations of several parts per million and comparable calcium concentration, the fraction of ammonium ion retained by the column at saturation would be practically negligible. This situation is generally typical of ion exchangers whereby the divalent ion is preferentially absorbed.

Methacrylic Acid Exchangers

In some preliminary experiments with fiber MS-WP-41A which contains polymethylmethacrylate (PMM), it was demonstrated that hydrolyzed PMM, i.e., polymethacrylic acid, can serve as a weak acid ion exchanger. The PMM was hydrolyzed and the polybutadiene in the fiber was crosslinked by exposure to concentrated sulfuric acid. Because of the presence of styrene in the fiber which was partially sulfonated by the sulfuric acid, the resulting ion exchanger was a combination weak acid and strong acid. The fiber had a total capacity of 1.0 meq/g and a salt splitting capacity of 0.3 meq/g. Thus, methacrylic acid accounted for 0.7 meq/g. Higher capacities should be possible with more complete hydrolysis of the polyester and with a greater fraction of ester in the fiber.

EVALUATION OF ANION EXCHANGE FIBERS

SDM Fibers

Fiber RF-PP-129D containing 60% styrene-dimethylaminopropylmaleimide (SDM) required 1.0 meq/g of HCl for complete neutralization. Based on the starting composition of the mixture to be spun the calculated capacity of SDM is 2.1 meq/g. The SDM was successfully crosslinked with 1,12-dibromododecane, but the resulting capacity was only 0.7 meq/g. Because of the low theoretical capacity of this SDM fiber and the still lower capacity actually obtained, further evaluation was discontinued in favor of working with materials having lower equivalent weights.

Vinylpyridine Fibers

Several attempts were made to crosslink fibers containing polyvinylpyridine (PVP) with epoxy resin (ER). In separate experiments with pure PVP it was demonstrated that ER and PVP react rapidly at 80°C. Thus, a controlled coating of ER on the fiber followed by heating to react the epoxy with the PVP could form a shell which would prevent loss of PVP but still allow for water permeability and a small amount of swelling. Alternatively the epoxy resin could be allowed to diffuse throughout the fiber prior to heating in order to obtain uniform crosslinking. Both the diffusion of the ER into the fiber and the attainment of a uniform coating of ER on the fiber were difficult to achieve. For example, a sample of MS-WP-2B was epoxy coated and cured at 75°C for an hour. The ion exchange capacity of the fiber decreased from 2.9 meq/g on the first exhaustion-regeneration cycle to 1.1 meq/g on the second cycle. Crosslinking by the epoxy coating method appears to be less desirable than treatment with dihaloalkanes because of the relative simplicity of the latter.

Fibers containing PVP were adequately crosslinked with mixtures of 1,6-dibromohexane and 1,12-dibromododecane but the capacities were generally low. For example, fiber MS-WP-12A (25% PP, 5% ABS, 70% PVP) treated with the dibromides gave a capacity of less than 1 meq/g. By first swelling the fiber with dilute HCl and then reacting it with an alkyl dibromide mixture, the capacity was improved to 1.9 meq/g. However, the swelling procedure resulted in some loss of the polyvinylpyridine before crosslinking was effected. Other swelling agents were sought in order to minimize the loss of vinylpyridine from the fiber. For example, a sample of MS-WP-12A was exposed to a solution of dibromohalides to which were added several drops of 2-pentanol. The fiber was then reacted with a n-heptane solution of 1-bromobutane and 1,10-dibromodecane; again several drops of 2-pentanol were added to swell the fiber. This treatment resulted in a total capacity of 3.2 meq/g and a salt splitting capacity of 1 meq/g. Further increases in capacities should be possible since a direct titration of fiber MS-WP-12A with HCl requires 3.6 meq HCl per gram of dry fiber.

A sample of MS-WP-12A was crosslinked with a mixture of 1,12-dibromododecane and 1,10-dibromodecane, quaternized with 1-bromobutane, finely cut, and placed in a column. The column was eluted with 0.025 N HCl, and the chloride ion concentration in the effluent was determined by silver nitrate titration. In the first elution with HCl the breakthrough capacity was 1.1 meq/g for an average flow rate of 1.6 ml/min. It was clear in the course of this elution that channeling was a serious problem - easily observed since the hydroxide and chloride forms have different colors. The fibers, 1 to 4 mm in length, were only loosely packed and in some places were matted. The column was therefore carefully repacked, the volume occupied by the fiber being reduced by nearly a factor of two. In the second elution at 1.8 ml/min the channeling was significantly diminished although still present. The breakthrough curve for this elution is shown in Figure 12. The breakthrough capacity

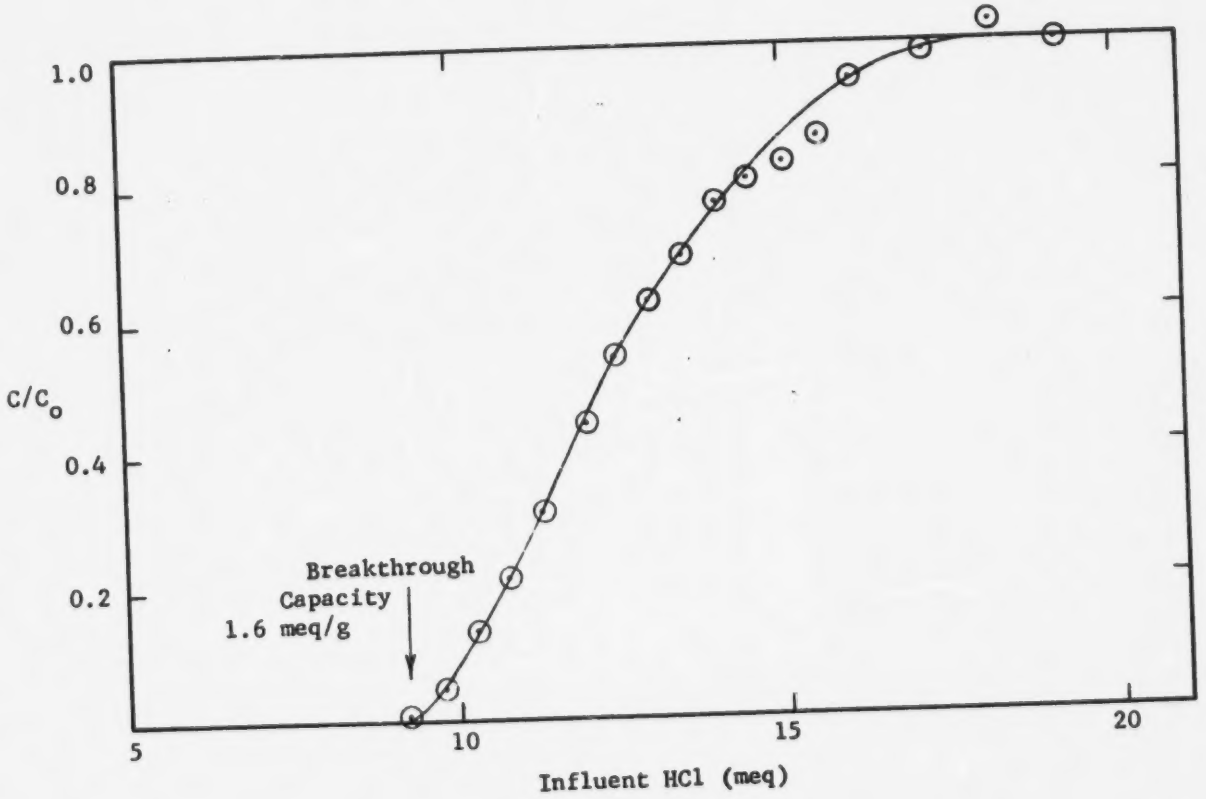

Figure 12

Breakthrough Curve for Anion Exchange Fiber (I-159)

is 1.6 meq/g; and the total capacity, determined from the area over the breakthrough curve, is 2.2 meq/g (dry fiber in the chloride form). A third elution at 0.5 ml/min resulted in the same breakthrough capacity as for the second elution at 1.8 ml/min. The breakthrough capacities were probably decreased considerably due to the poor packing of the fibers in the column.

Improvement in packing efficiency was made by decreasing the average fiber length to about 1 mm. Total capacity was increased by crosslinking with lower molecular weight alkyldihalides and by using fiber with a higher fraction of PVP. Thus, a finely cut sample of fiber MS-WP-4B (15% PP, 5% PS, 80% PVP) was crosslinked with a heptane solution of 1,6-dibromohexane and further quaternized with a n-butyl bromide. A 4 g sample of this fiber, packed in a 100 ml buret, occupied about 5.4 ml/g fiber. The large volume to weight ratio was mainly attributable to poor packing efficiency rather than swelling. The column was eluted at flow rates from 3.5 ml/min to 24.9 ml/min with 0.02 N HCl. A maximum capacity of 2.9 meq/g was found for this sample. The breakthrough curves are shown in Figure 13. In general, the breakthrough curves are normal in that the efficiency of ion exchange increases with decreasing flow rates. However, as seen from Table 14, the total capacity decreased with the number of elutions or alternatively the total capacity decreased with increasing flow rate. The reason for this behavior could not be ascertained since the column was dismantled after the third elution.

Fiber MS-WP-12E (15% PP, 5% ABS, 80% PVP) yielded the highest capacity of all anion exchange fibers tested. Short lengths of the fiber were obtained by cutting a knitted sample of the drawn fiber. The fiber was then crosslinked in a decane solution of 1,6-dibromohexane and 1,10-dibromodecane (seven days at 45-55°C). After washing with methanol and drying, the sample was placed in a column (sample No. II-52). The results of an elution with 0.0157 N HCl are shown in Figure 14. The breakthrough capacity is about 86% of the total capacity, 3.81 meq/g. The higher breakthrough capacity was a result of improved column packing efficiency (less than 4 ml/g fiber).

Selectivities for Vinylpyridine Fibers

Sample II-52 (MA-WP-12E) was eluted with a solution containing both chloride 0.0190 N and phosphate 0.0012 N $H_2PO_4^-$) at pH $\approx$ 1.7. The results of this elution are shown in Figure 15 for chloride ion and Figure 16 for phosphate ion. At this acidity the phosphorus is assumed to consist almost entirely of the monovalent ion, $H_2PO_4^-$. In this case the selectivity is highly in favor of chloride ion. Pertinent data for this elution is given in Table 14.

The influent solution for the third elution of sample II-52 also had phosphate and chloride ion, the pH of the solution being about 2.6. Breakthrough curves for chloride and phosphate ions are shown in Figures 17 and 18, respectively. Examination of the results for this elution (Elution No. 3 in Table 14) show that if the sorbed phosphorus

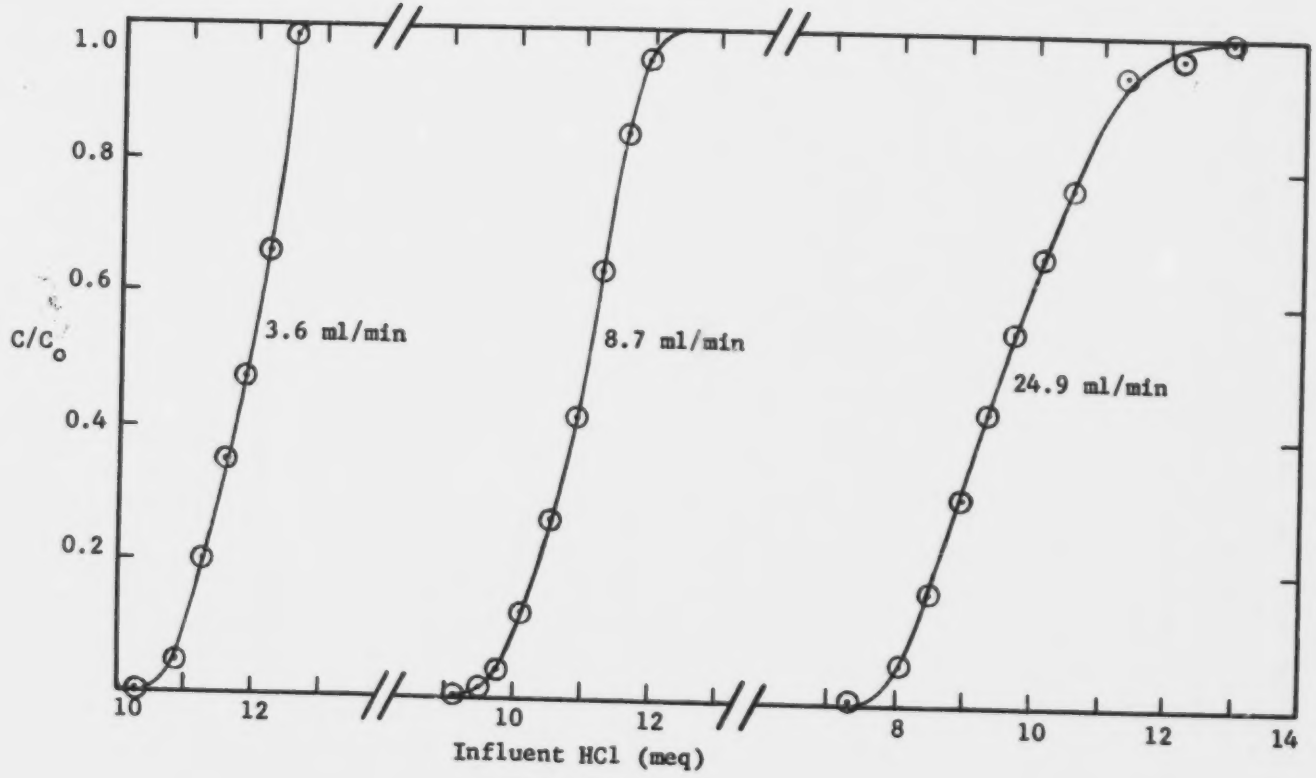

Figure 13

Breakthrough Curves for Anion Exchange Fiber II-2

Table 14

Elutions for Anion Exchange Fiber II-52

Elution No.	1	2	3	4	5	6	7	8
Chloride Absorbed on Column (meq)*	13.72	13.91	6.88	13.49	13.41	13.41	3.62	6.51
Phosphate Absorbed on Column (mm)**		0.25	3.68					
Nitrate Absorbed on Column (meq)							9.79	6.90
Chloride Conc. (meq/liter)	15.66	18.96	3.544	15.73	15.73	15.73	8.221	3.637
Phosphate Conc. (mm/liter)		1.25	3.196					
Nitrate Conc. (meq/liter)							10.28	4.548
Total Capacity (meq/g)	3.82	3.9	3.7	3.74	3.73	3.73		
$K^{Cl}_{H_2PO_4}$		3.62						
$K^{Cl}_{HPO_4}$			0.0033					
$K^{NO_3}_{Cl}$							2.2	0.85
Ave. Elution Rate (ml/min.)	12.4	15.6	13.6	16.7	13.5	12.3	14.1	14.7

*meq = milliequivalents
**mm = millimoles

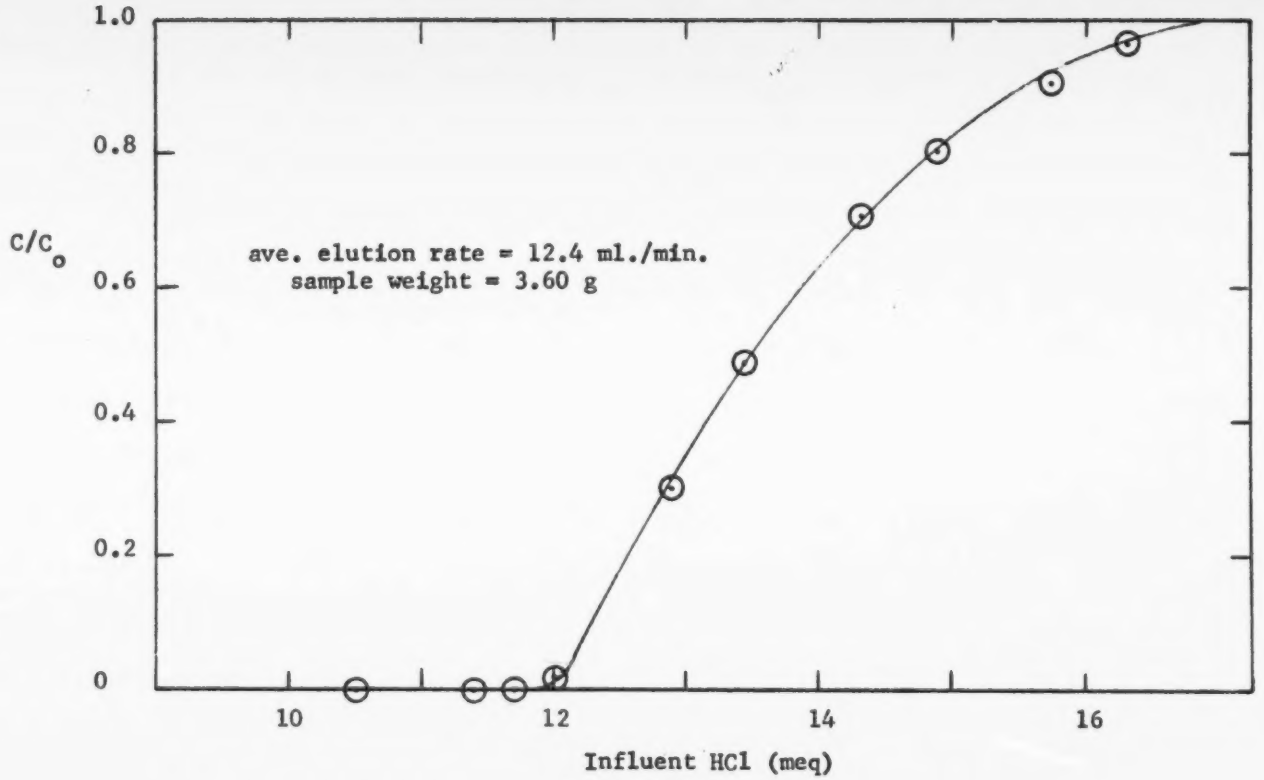

Figure 14

Breakthrough Curve for Anion Exchange Fiber II-52 (MS-WP-12E)

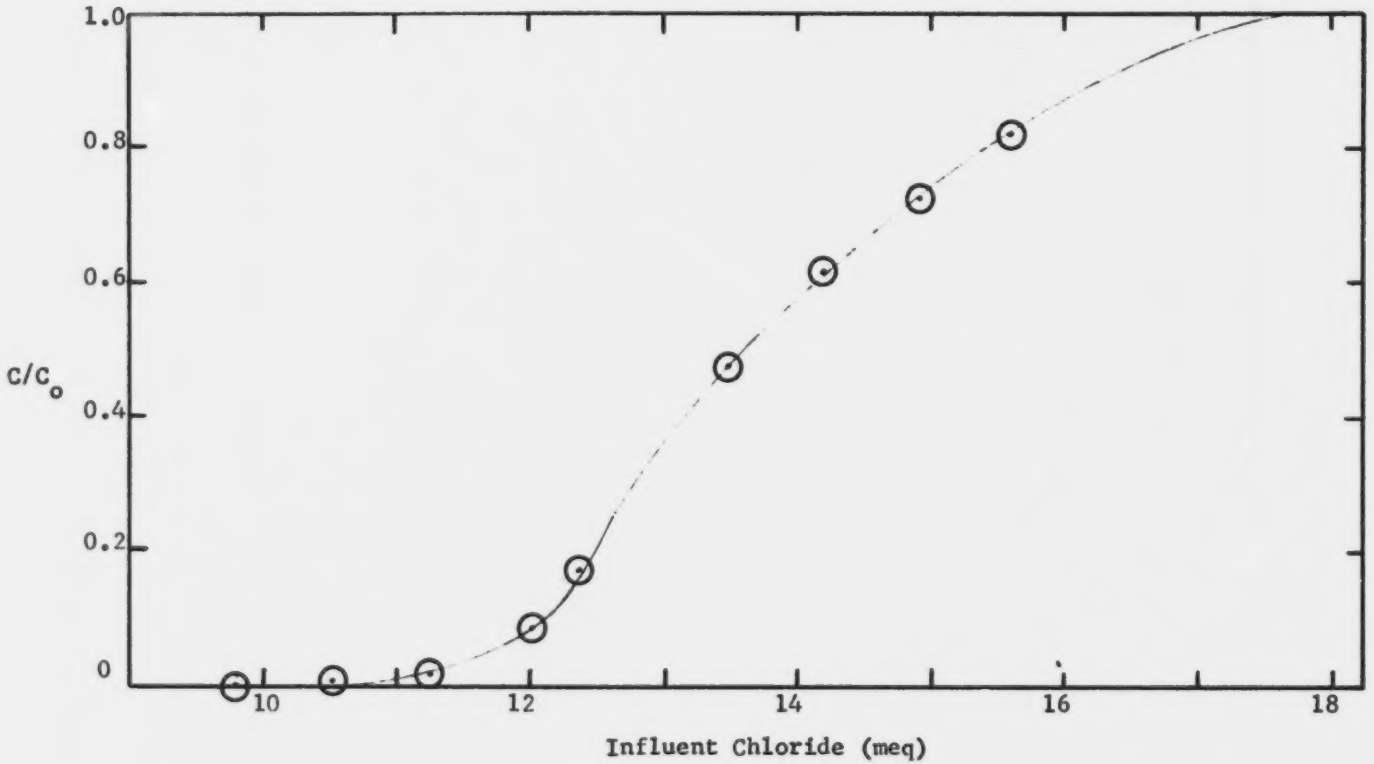

Figure 15

Chloride Ion Breakthrough for Second Elution of Sample II-52

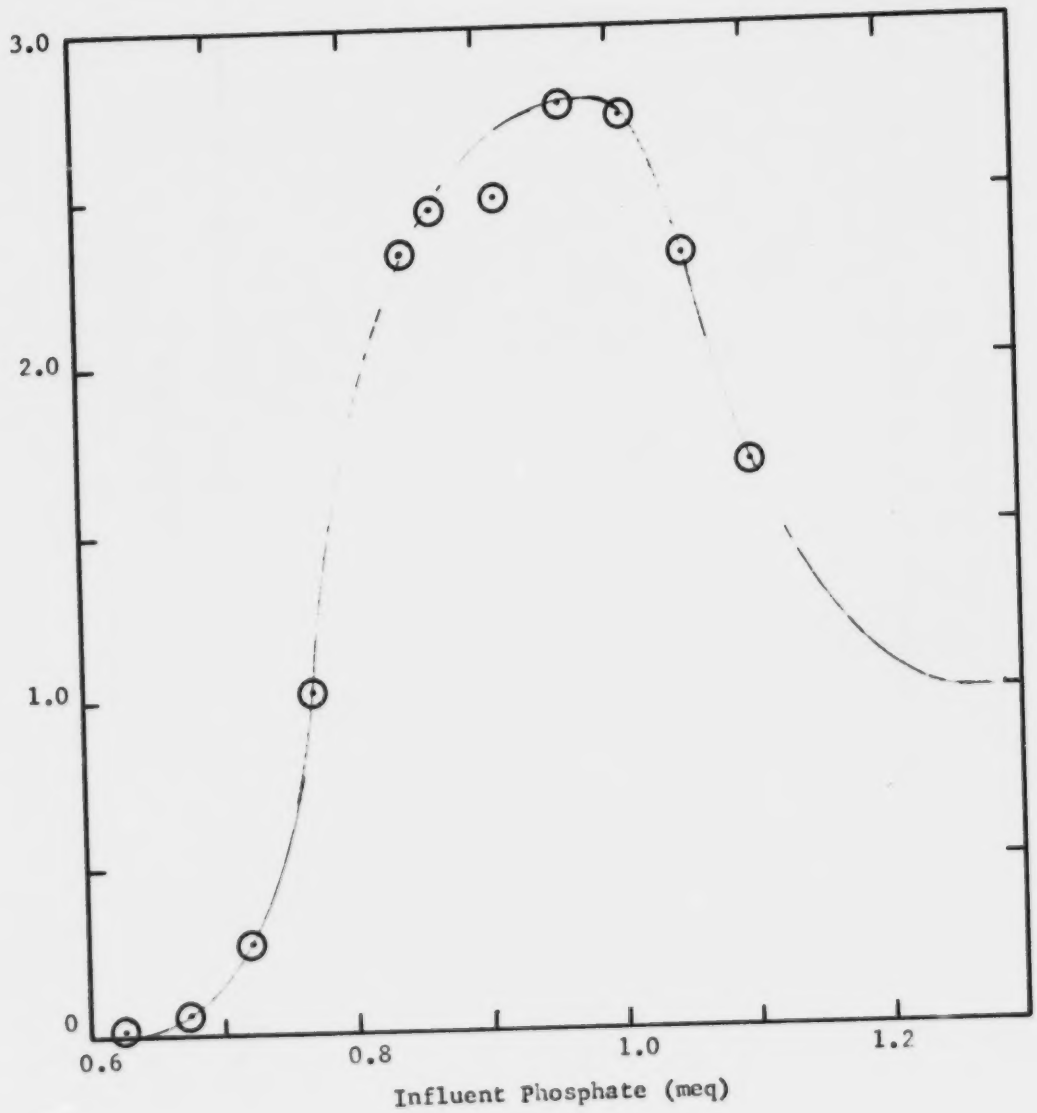

Figure 16

Phosphate Ion Breakthrough for Second Elution of Sample II-52

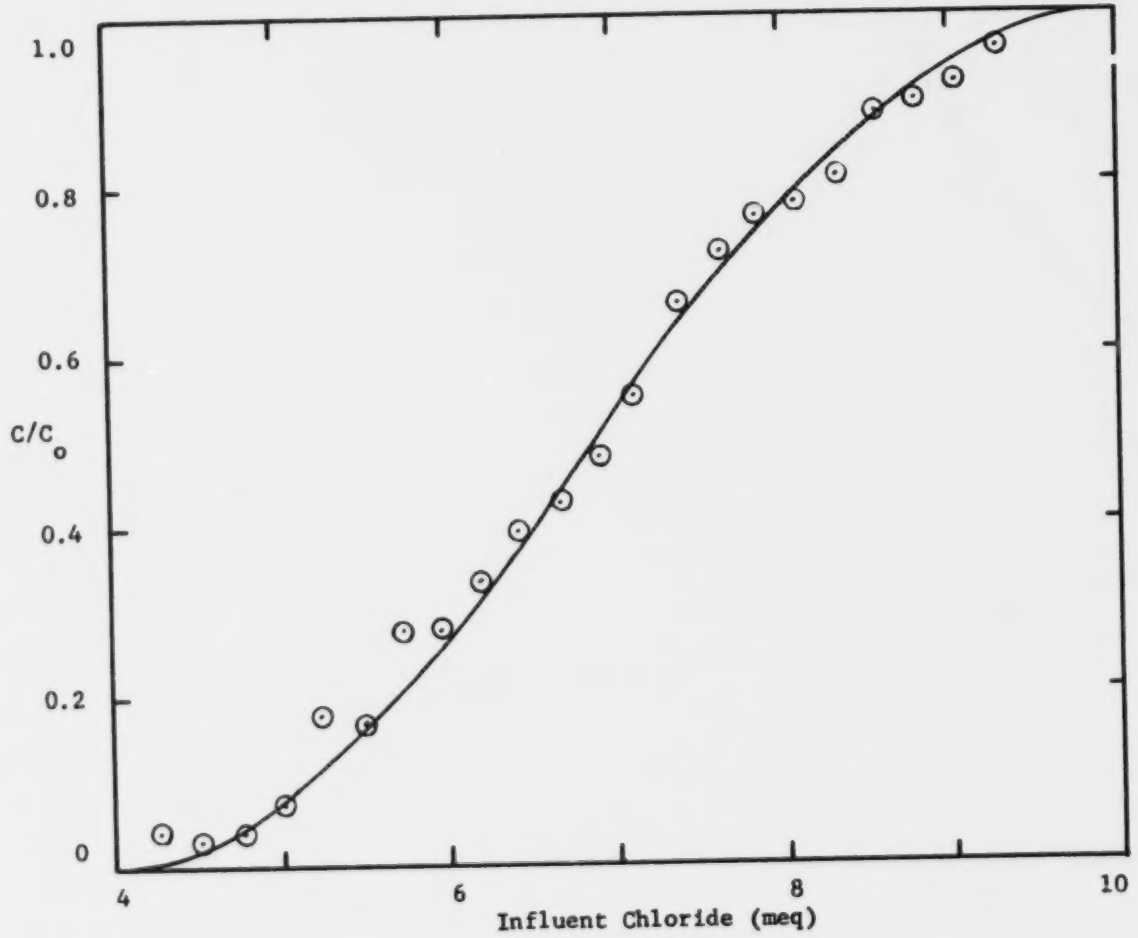

Figure 17

Chloride Ion Breakthrough Curve for Third Elution of Sample II-52

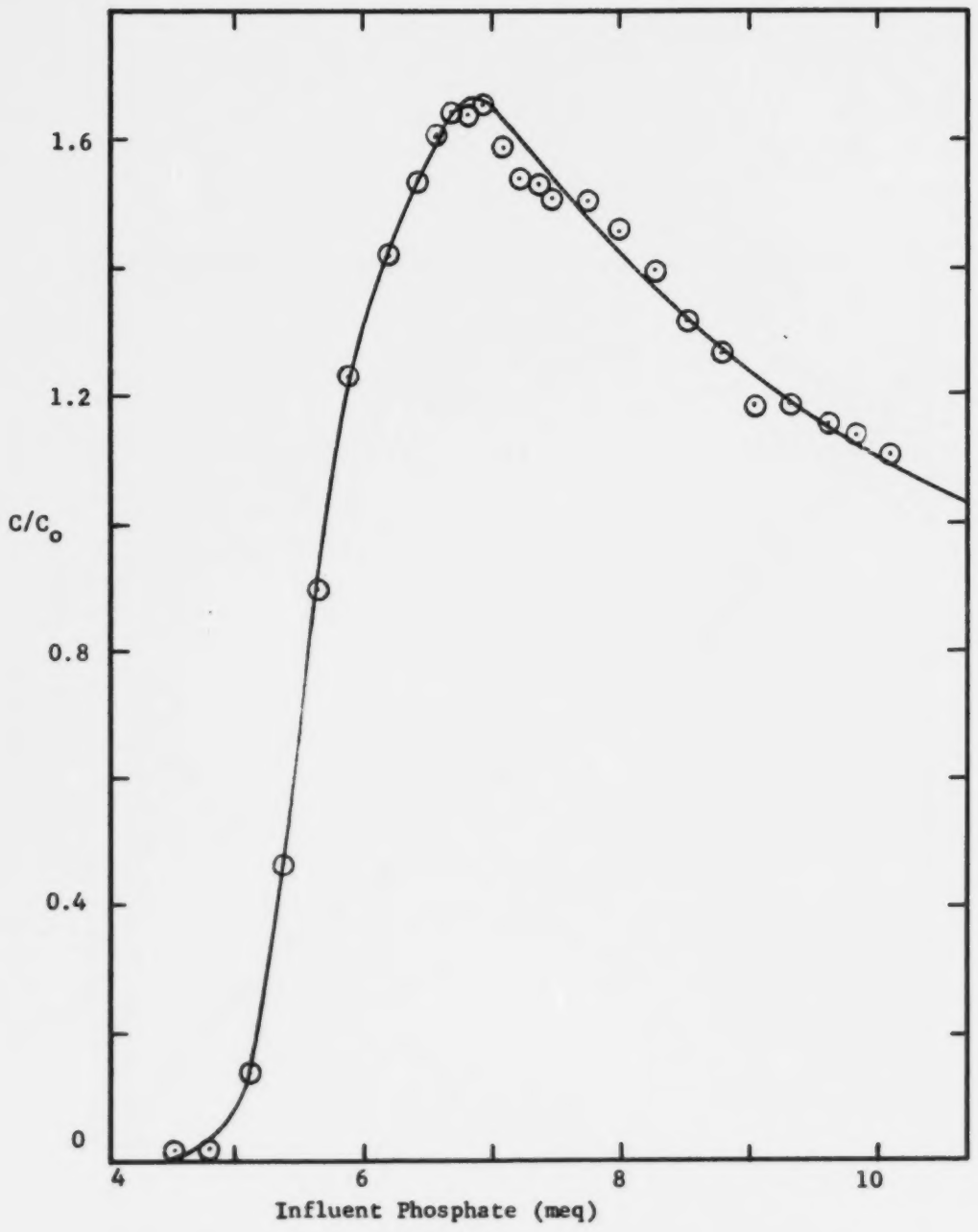

Figure 18

Phosphate Ion Breakthrough Curve for Third Elution of Sample II-52

is considered to be in the monovalent ion state, $H_2PO_4^-$, the total capacity of the fiber is 2.9 meq/g. However, if the phosphorous is in the divalent ion state, $HPO_4^=$, the total capacity, 3.7 meq/g, conforms more closely to the capacities obtained in the first two elutions. Therefore, it is assumed that the divalent ion predominates on the exchanger, and the selectivity coefficient is accordingly calculated for $HPO_4^=$. As expected the selectivity increasingly favors the phosphate ion over chloride as the pH is increased since ions of higher valence are preferentially absorbed.

Elutions 4 through 6 of sample II-52 are shown in Figures 19 to 21. The purpose of these elutions with 0.0157 N Cl^- was to check the stability of the total capacity of the fiber. A meaningful estimation of the lifetime of the ion exchange fiber is not possible from the elutions of Table 14. On the other hand, in elutions 4, 5, and 6 there is no indication of serious attrition. Between elutions 1 and 4 there is a 2% decrease in capacity, but this is not uncommon in any type of ion exchanger.

The influent solution for the seventh elution contained chloride and nitrate ions. Since the nitrate ion breakthrough curve was not determined, the total capacity from the sixth elution was utilized in order to determine the steady state absorption of nitrate ion on the column. The breakthrough curve for chloride ion is shown in Figure 22. Selectivity is seen to be in favor of the nitrate ion. In the eighth and final elution both chloride and nitrate ions were again present but in lesser concentrations. The ratio of chloride to nitrate ion is constant in elutions 7 and 8. Figure 23 gives the chloride ion breakthrough curve for the eighth elution. As with the seventh elution, the nitrate absorbed on the column was taken as the difference between the total chloride absorbed in the sixth elution and the chloride absorbed in the eighth elution. In this case chloride ion is preferentially absorbed by the fiber. This preference would probably prevail at still lower concentrations.

From the results of the above elutions of sample II-52 (MS-WP-12E), the properties of the vinylpyridine anion exchange fiber are seen to be typical of common commercial ion exchangers, although the capacities are generally somewhat lower. No physical deterioration of the fiber was detected after the eighth elution.

Polyethyleneimine Fibers

In the evaluation of fiber MS-WP-44A containing 10% polyethyleneimine (PEI), it became apparent that PEI is not as easily rendered water insoluble by dibromoalkanes as is polyvinylpyridine. Initial cross-linking attempts led to almost complete extraction of the PEI in acidic solution. By prolonged heating of the fiber in dibromoalkane solution the loss of PEI in acidic medium was considerably but not completely reduced. The column evaluations of these samples are described below.

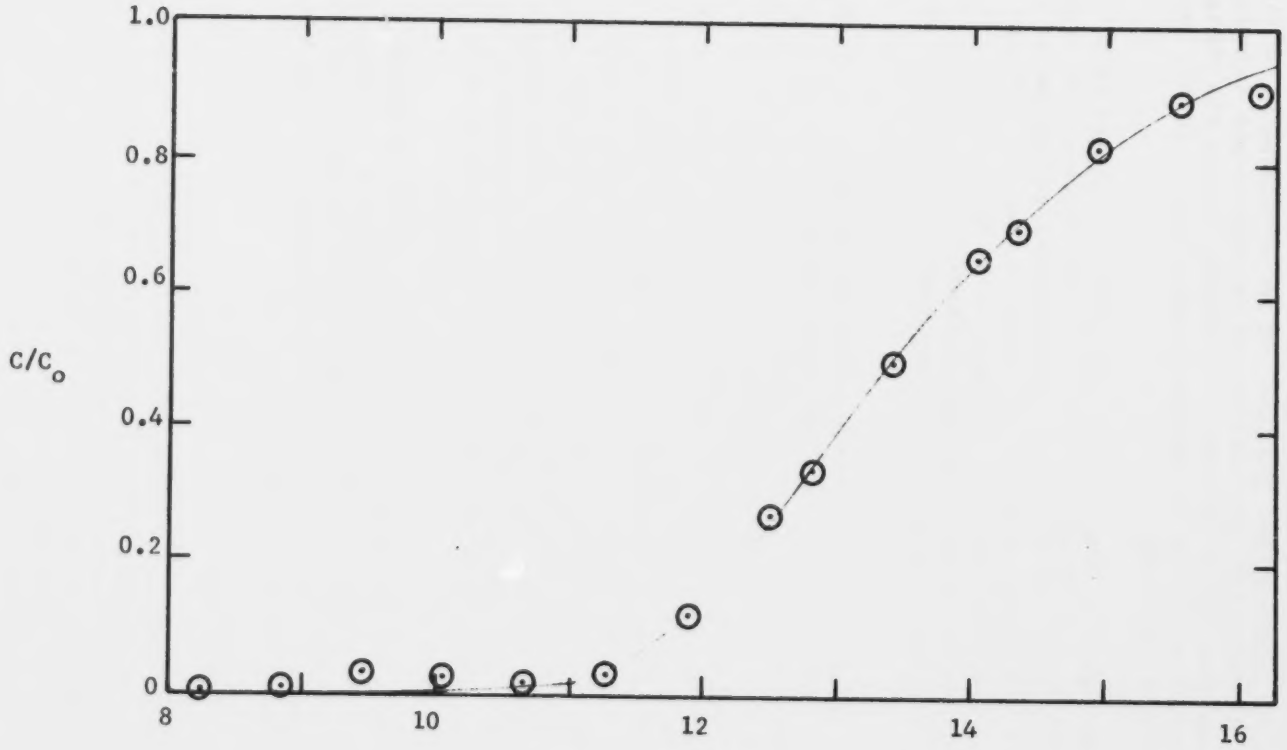

Figure 19

Fourth Elution of Sample II-52

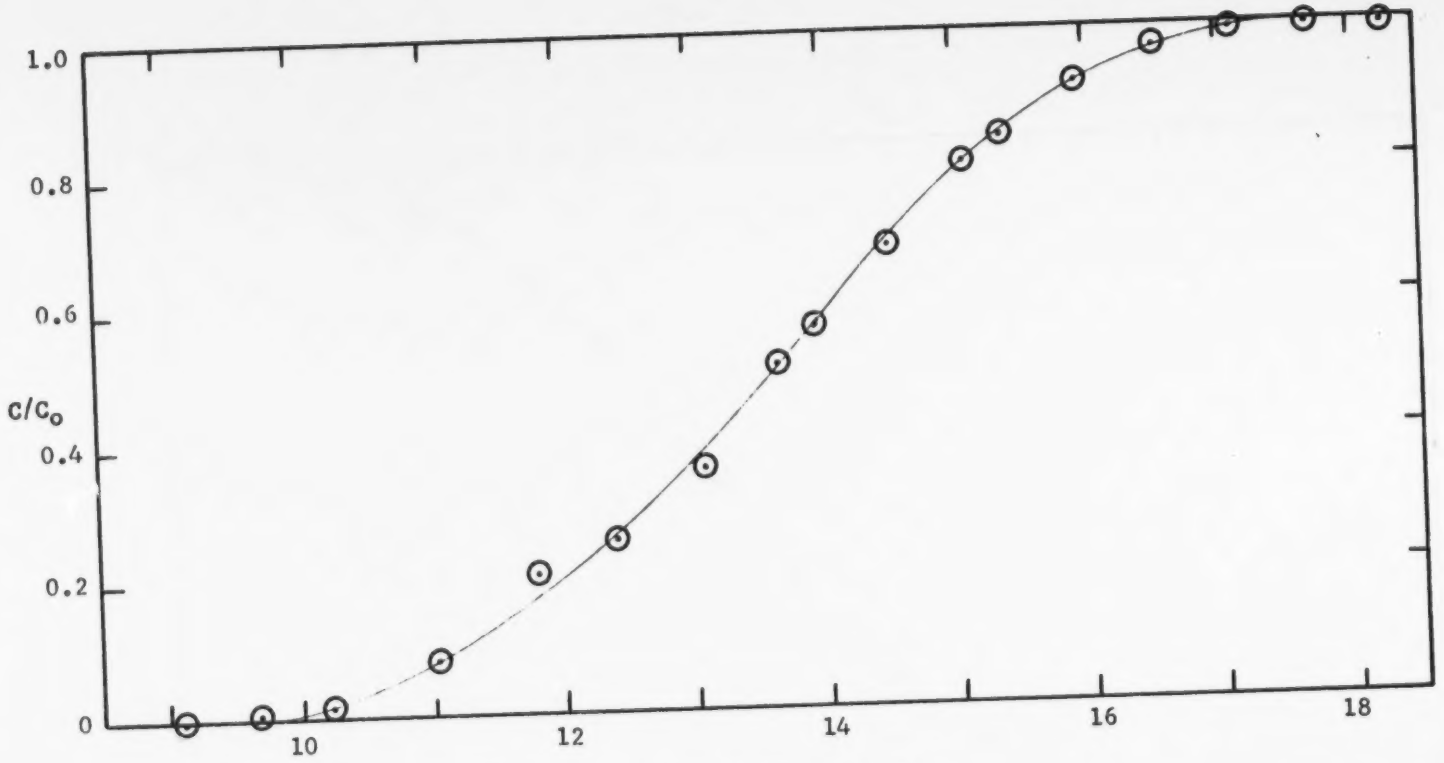

Figure 20

Fifth Elution of Sample II-52

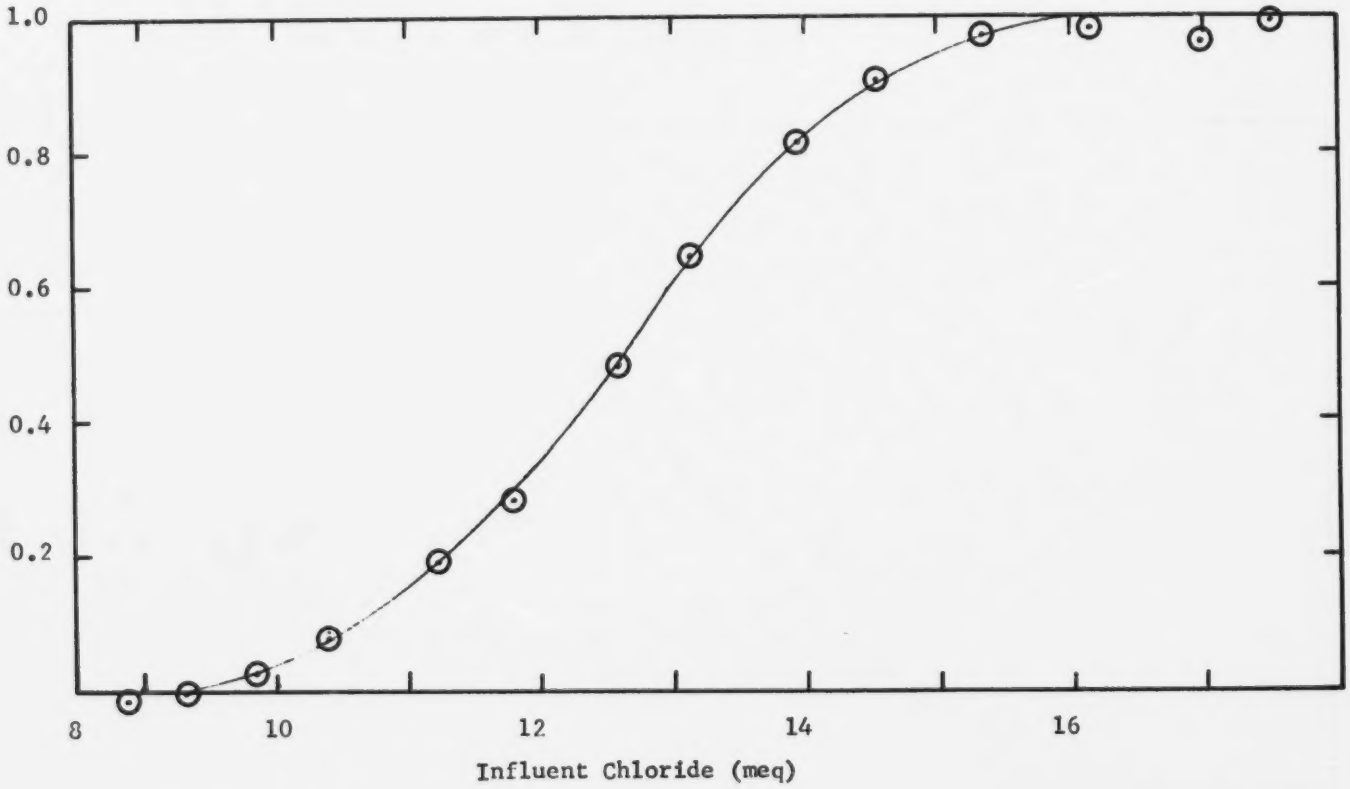

Figure 21

Sixth Elution of Sample II-52

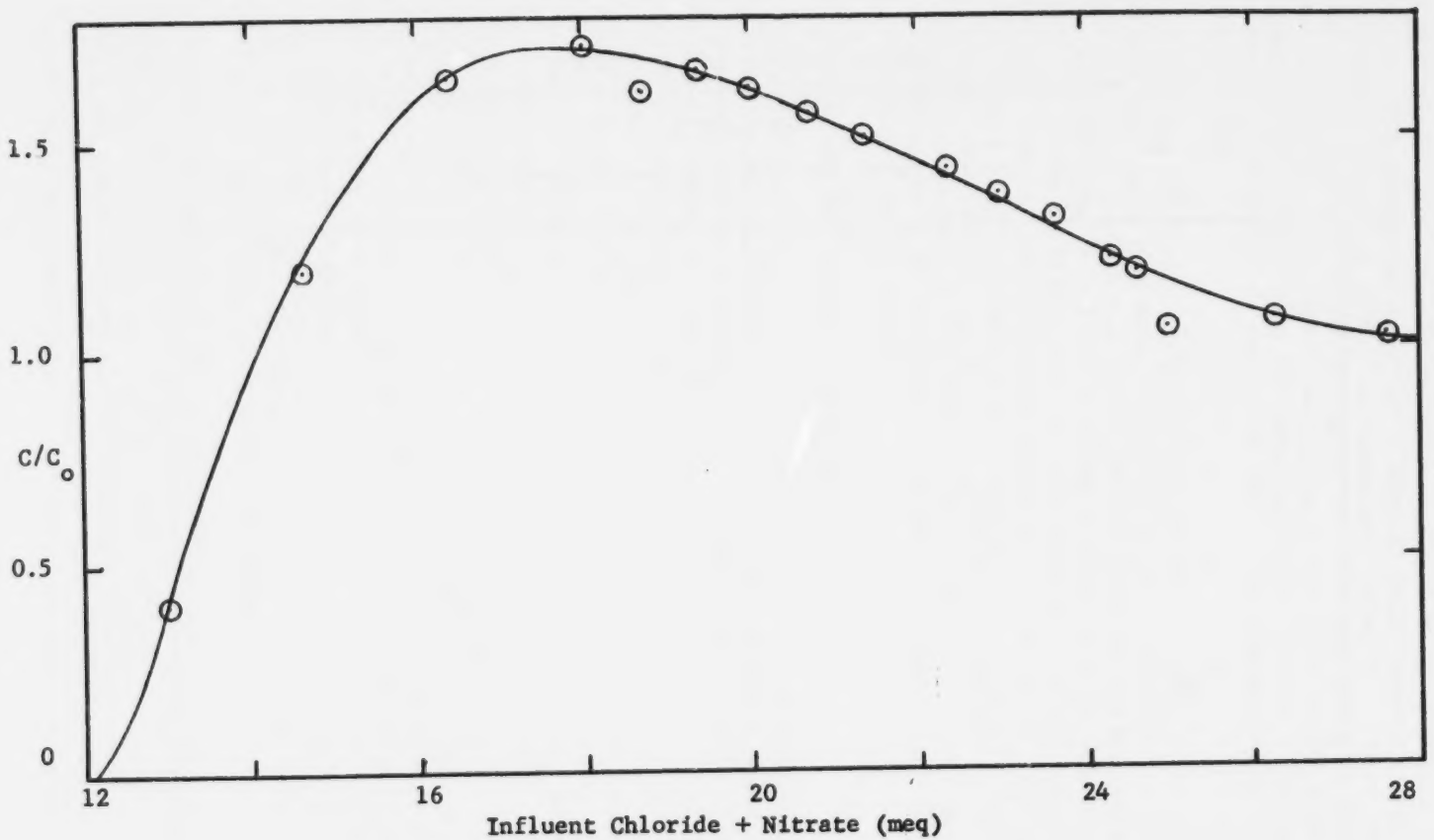

Figure 22

Chloride Ion Breakthrough Curve for Nitrate-Chloride Elution of Sample II-52, Seventh Elution

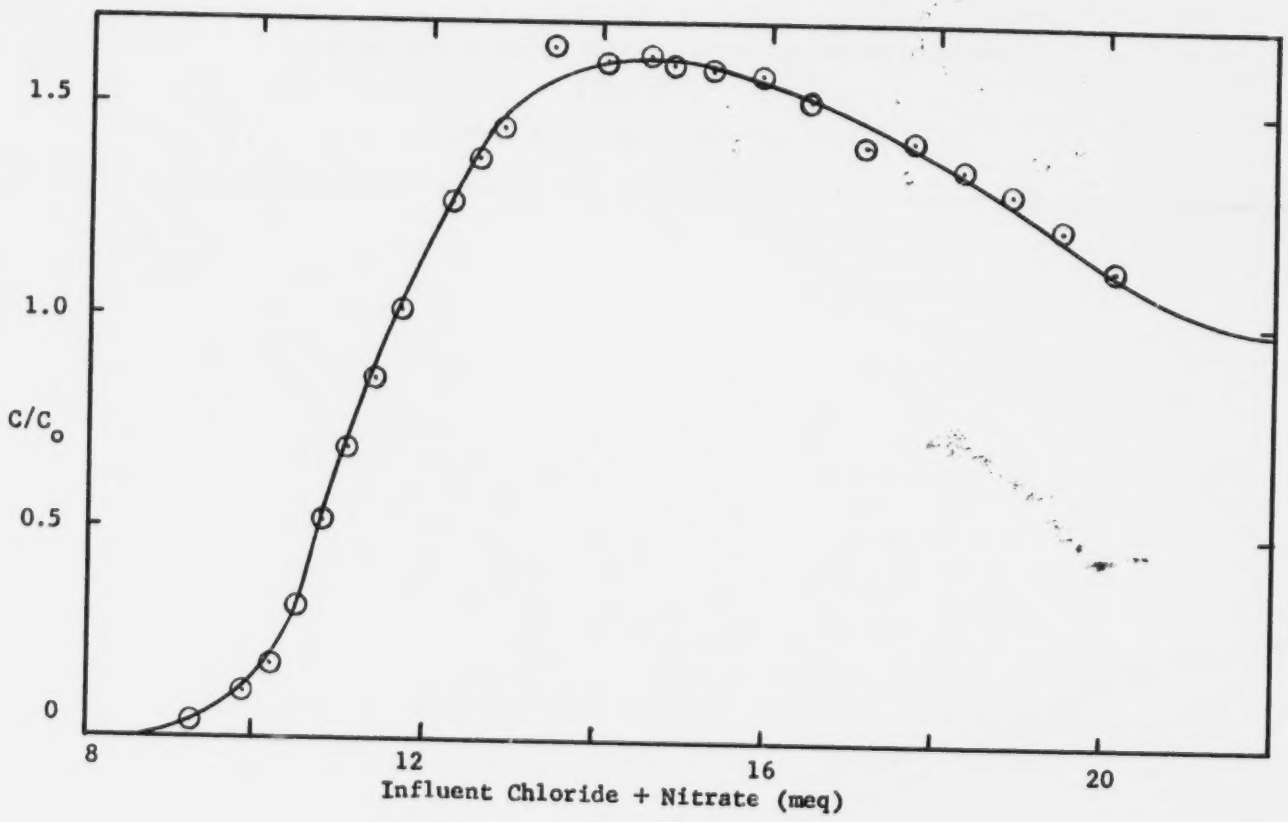

Figure 23

Chloride Ion Breakthrough Curve for Nitrate-Chloride Elution of Sample II-52, Eighth Elution

Sample II-37 (from finely cut MS-WP-44A) was treated with a 5% dibromohexane, 95% decane solution for 8 days at room temperature and an additional 2 days at 50°C. An exemplary column elution of this fiber with 0.016 N HCl is shown in Figure 24. The low breakthrough capacity for this fiber, less than 2 meq/g, is a result of inefficient packing; breakthrough of more than 10% occurred above 3 meq/g. The total capacity, 3.4 meq/g, is quite low due to the extraction of PEI during the elutions.

Another sample (II-55) of MS-WP-44A was treated with a 10% dibromohexane, 5% dibromodecane, 85% decane solution at 45 to 50°C for a week after which n-butyl bromide was added and the solution was maintained at 50° for an additional 5 hours. A column elution of this sample with 0.02013 N HCl is shown in Figure 25. In this case the breakthrough capacity exceeds 3 meq/g, and the total capacity, 3.6 meq/g, is an improvement over sample II-37. Nevertheless, this fiber should have a greater capacity than the 3.8 meq/g obtained from fiber MS-WP-12E (e.g., sample II-52) since both have 80% PVP for MS-WP-12E. A second elution of sample II-55 with 0.02 N HCl is shown in Figure 26. Again the total capacity of the sample is 3.6 meq/g.

Selectivities for Polyethyleneimine Fibers

With the establishment of a reasonably stable total capacity (i.e., no further extraction of PEI), sample II-55 was eluted a third time with a phosphate-chloride solution. The results of this elution are given in Figure 27. Because the elution was stopped before a steady state condition had been reached, the extrapolation necessary to approximate attainment of the steady state (dashed line of Figure 27) introduces a sizable error in the determination of phosphate absorption on the column. However, it is still possible to determine the selectivity coefficient within about 25% error. Selectivity is clearly in favor of the chloride ion (see Table 15). It is predicted that the selectivity coefficient would not vary greatly as the total ion concentration is reduced (at constant pH) since the ratio of activity coefficients would be nearly constant for the dilute solutions being considered. On the other hand, a change in relative concentrations of chloride and phosphate ions will affect the selectivity coefficient. Generally the selectivity coefficient decreases as the fraction of ion preferentially absorbed (chloride) increases; however, experiments to confirm this relationship have not been performed. It should be noted that the phosphate-chloride solutions used in the elutions for Table 15 had a pH of 1.7; at this acidity the monovalent anion $H_2PO_4^-$ is probably absorbed.

A finely cut sample (II-63) of fiber MS-WP-44D (15% pp, 5% ABS, 50% PVP, 30% PEI) was exposed to a decane solution of 1,6-dibromohexane and 1,10-dibromodecane for 14 days at 50°C. After the second day, 1-bromobutane was added. Although the prolonged treatment with dibromoalkanes provided more extensive crosslinking than previously obtained with fibers containing PEI, part of the fiber was still soluble in dilute

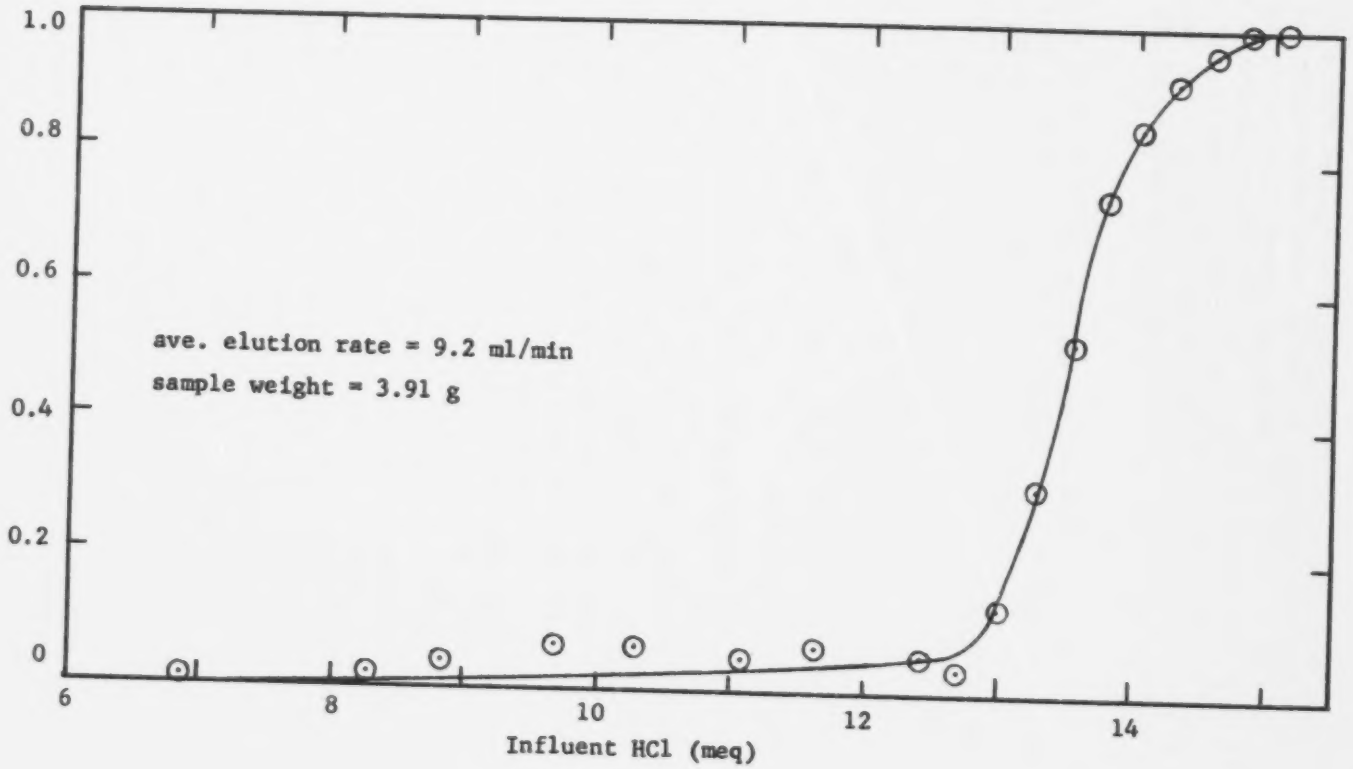

Figure 24

Breakthrough Curve for Anion Exchange Fiber II-37 (MS-WP-44A)

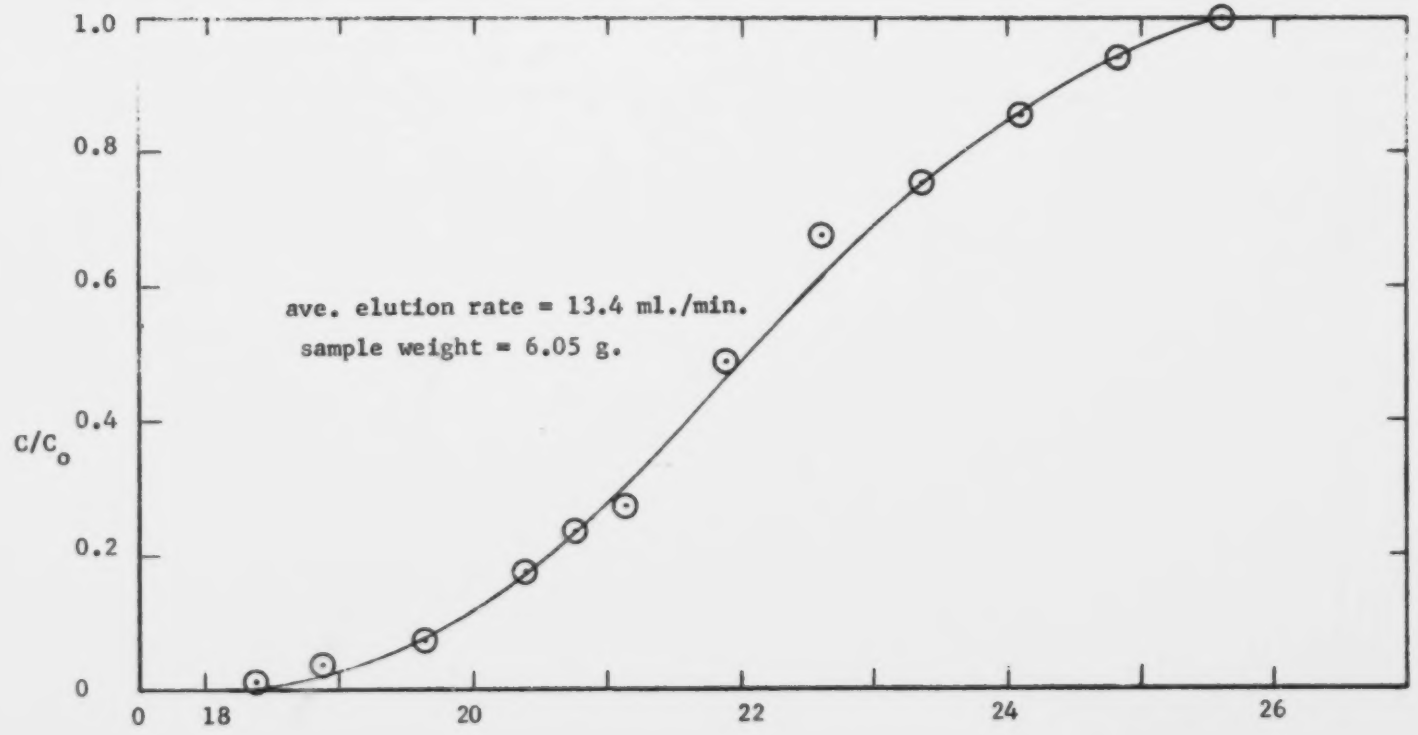

Figure 25

Breakthrough Curve for Anion Exchange Fiber II-55 (MS-WP-44A)

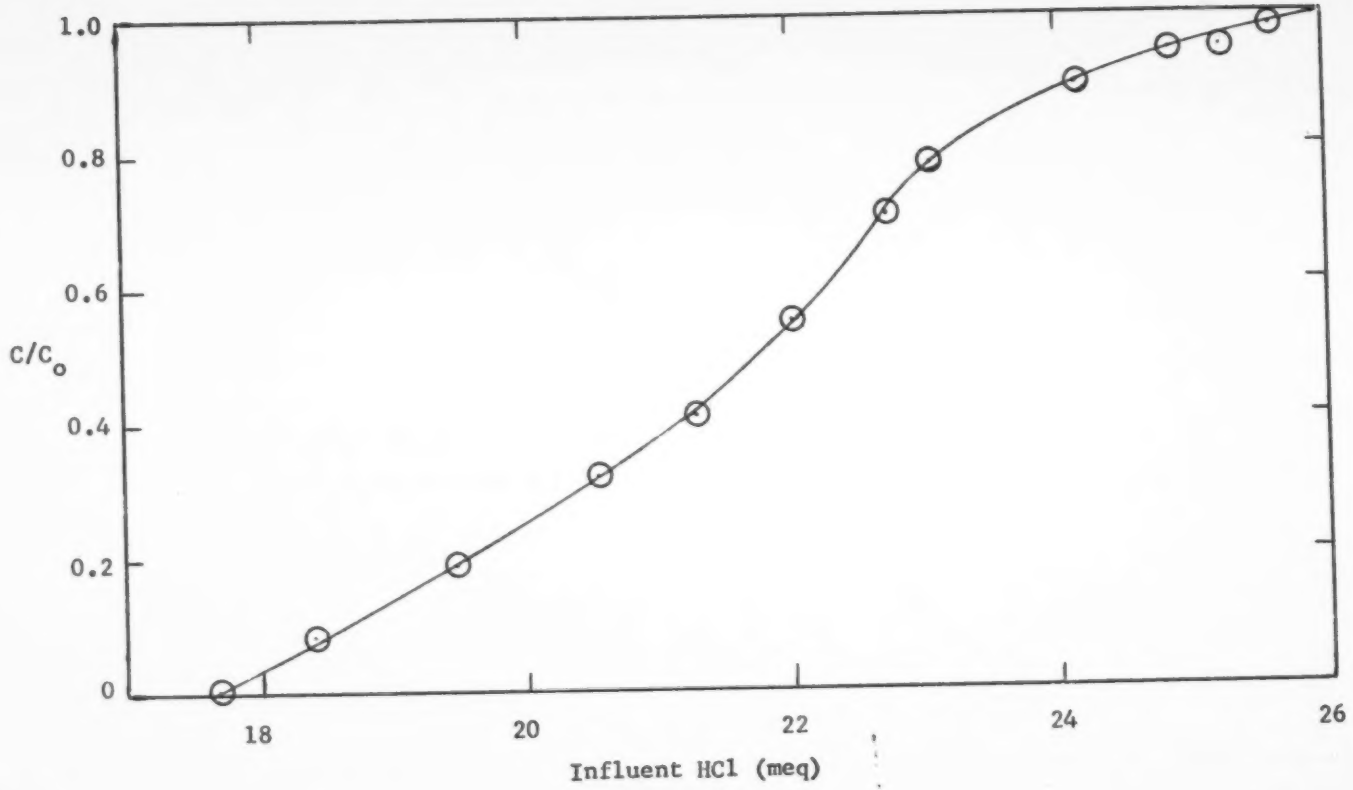

Figure 26

Second Elution of Sample II-55

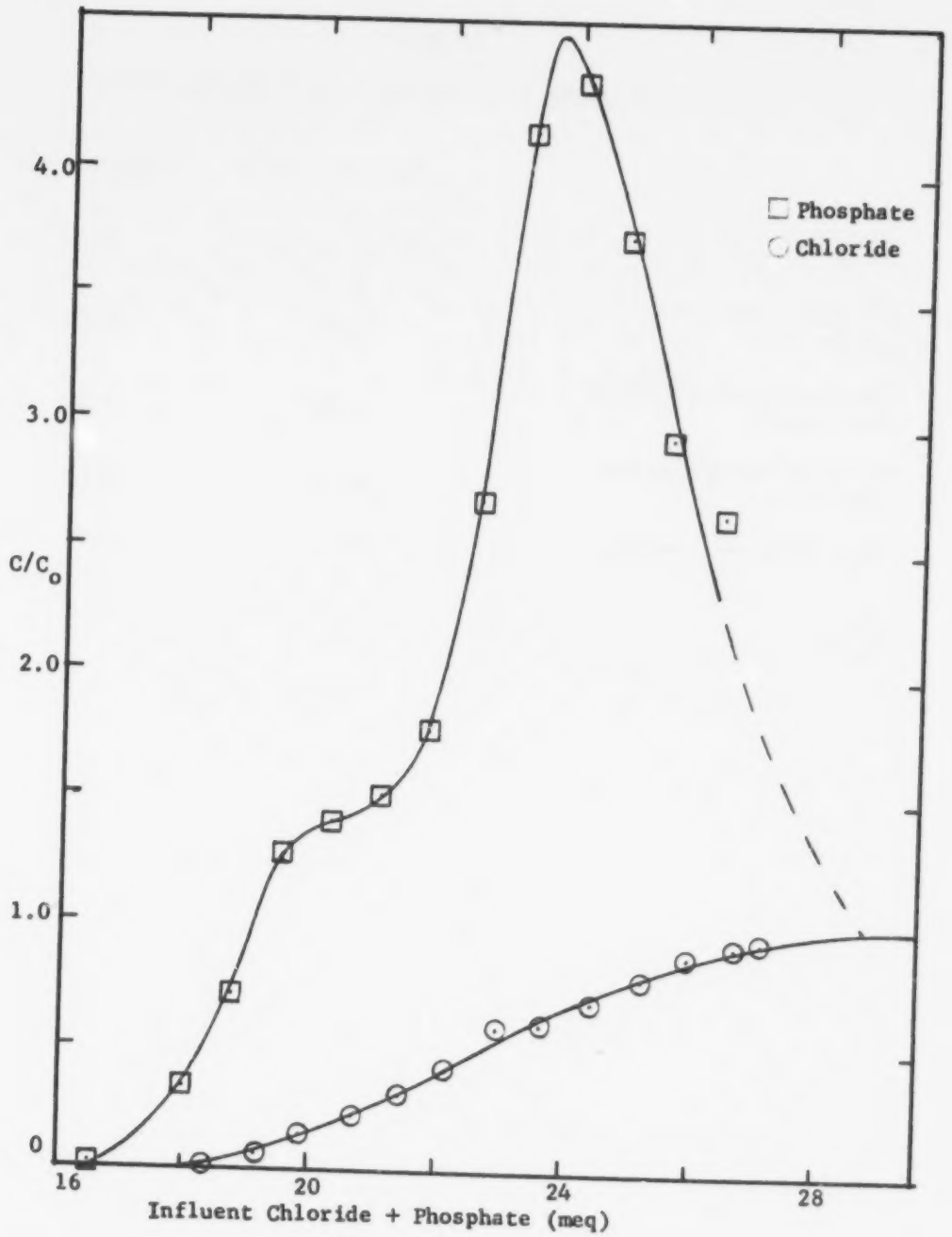

Figure 27

Third Elution of Sample II-55 (Chloride + Phosphate)

Table 15

Phosphate-Chloride Elutions of Anion Exchange Fibers

	Sample II-55	Sample II-63
Phosphate Absorbed on Column (meq)	0.23 ± .06	0.25
Chloride Absorbed on Column (meq)	21.97	18.50
Phosphate Concentration (meq/liter)	1.28	1.22
Chloride Concentration (meq/liter)	18.96	18.96
Total Capacity (meq/g)	3.7	3.6
$K^{Cl}_{H_2PO_4}$	6.5 ± 1.5	4.8

acid. Nevertheless, even with the loss of PEI the total capacity was in excess of 3.5 meq/g which indicates that at least part of the PEI was rendered insoluble. This is about the same capacity as obtained from the fiber having 80% PVP. Thus, if extraction of PEI can be prevented, higher capacities should be possible.

Sample II-63 (MS-WP-44D) was also eluted with a chloride-phosphate solution. The results of this elution are shown in Figure 28 and Table 15. Within the experimental error the selectivity is the same as for sample II-55. Since samples II-55 and II-63 both contain the same components but in different proportions, the selectivity coefficients are expected to be nearly equal.

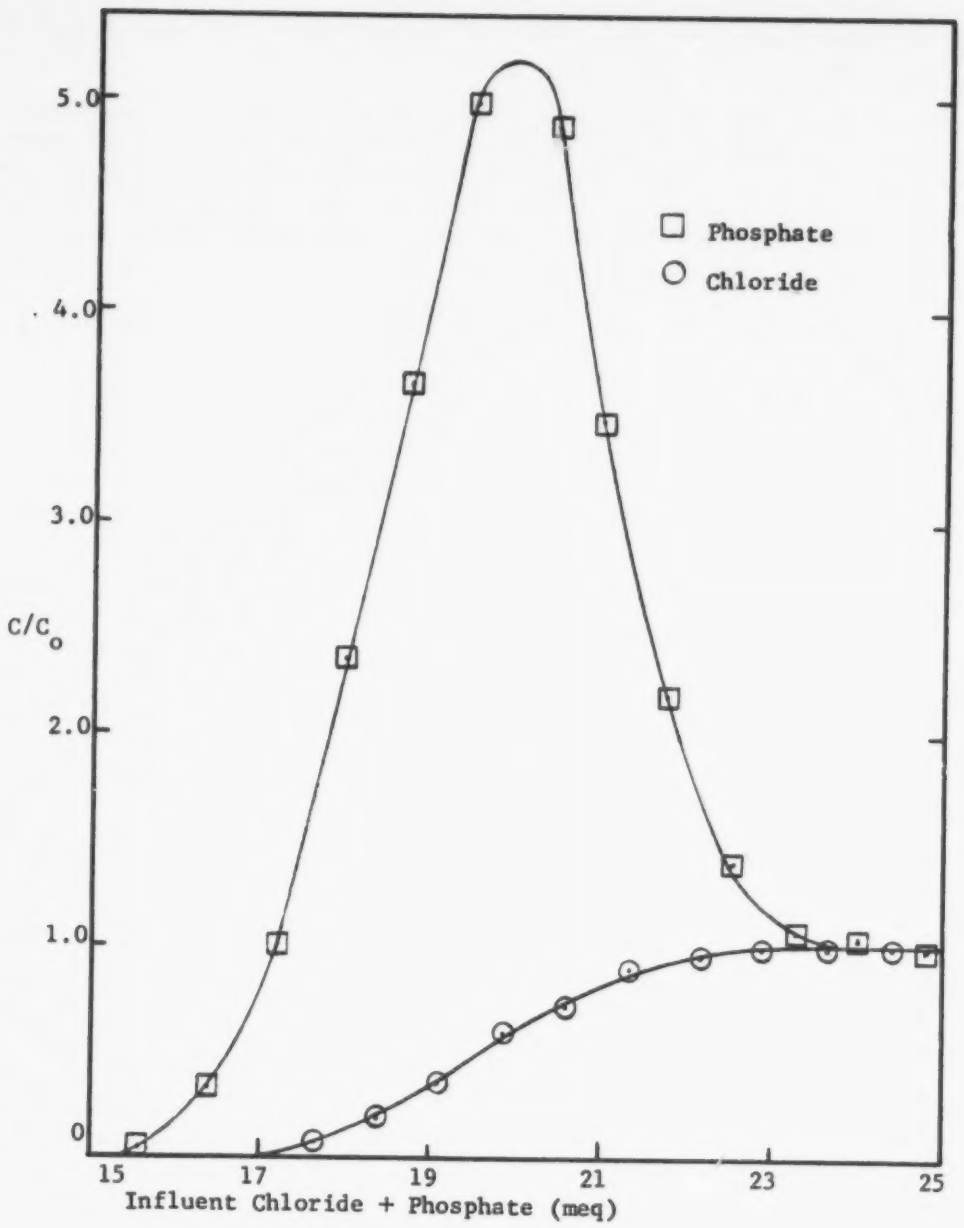

Figure 28

Phosphate-Chloride Elution of Sample II-63

SECTION VI

ACKNOWLEDGMENTS

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SECTION VII

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SECTION VIII

GLOSSARY

Materials Used in Fiber Mixtures

ABS	acrylonitrile-butadiene-styrene (16:7:77 polymer blend) Dow "Tybrene"
EMA	sodium salt of ethylene-methacrylic acid copolymer, DuPont "Surlyn 1559"
ER	epoxy resin, Dow "DER 662"
GMA	copolymer of methyl vinyl ether and maleic anhydride, GAF "Gantrez AN 169"
NBR	15:85 copolymer of acrylonitrile and butadiene, Arco "Poly BD, CN-15"
NPA	Nylon-6 polyamide
NW	alkylated p-cresol type antioxidant, Uniroyal "Naugawhite"
PAA	polyacrylic acid, Rohm & Haas Acrysol
PAAS	sodium salt of PAA
PAS	polyaminostyrene (Norsk Hydro)
PEI	polyethyleneimine, Dow PEI-1000
PMM	methyl methacrylate-styrene-butadiene, Rohm & Haas "Acryloid"
PMS	polymethylstyrene, Amoco Resin 18
PP	polypropylene
PPP	peroxidized polypropylene
PS	polystyrene
PVP	1:1 copolymer of 2-vinylpyridine and 2-methyl-5-vinylpyridine
PVP-HAc	PVP neutralized with acetic acid
SB-1	9:1 copolymer of styrene and butadiene
SB-2	8:2 copolymer of styrene and butadiene
SB-3	72:28 copolymer of styrene and butadiene

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GLOSSARY (contd.)

SBR	1:3 styrene-butadiene copolymer, Arco "Poly BD, CS-15
SDM	styrene-dimethylaminopropyl maleimide copolymer
SMA-1	1:1 copolymer of styrene and maleic acid, Arco Chemical Co.
SMA-2	2:1 copolymer of styrene and maleic acid, Arco Chemical Co.
SVP	3:7 copolymer of styrene and 2-vinylpyridine

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16. Abstract

The feasibility of making fibers which have the ability to sorb minerals from water has been investigated. High molecular weight organic polymers cospun with fiber-forming polymers and crosslinking agents can be spun into fiber and chemically treated to give ion exchanging materials. In some cases the ion exchange active material can be spun directly (e.g.. polyamines and polyvinylpyridines); in other cases the activity must be introduced after spinning (e.g., the sulfonation of fibers containing polystyrene).

Styrene sulfonic acid cation exchange fibers having capacities up to 4.2 meq/g dry fiber have been prepared. Polypropylene and polybutadiene served as fiber-forming polymer and crosslinking agent, respectively.

Weak acid cation exchangers were produced from fibers containing polymethyl-methacrylate by hydrolysis of the ester to polymethacrylic acid. Capacities up to 1 meq/g were obtained.

Vinylpyridine and aliphatic amine ion exchange active materials were spun directly and then crosslinked with dihaloalkanes. Quaternization was achieved with alkyl halides. Vinylpyridine exchangers gave capacities up to 3.8 meq/g, and fibers containing both vinylpyridine and polyethyleneimine show promise of yielding higher capacities.

17a. Descriptors

*Ion Exchange Fiber
*Capacity
*Selectivity
*Fiber Spinning

17b. Identifiers

*Ion Exchange
*Demineralization

17c. COWRR Field & Group 05D

18. Availability

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